



# Treatment of electroplating industry wastewater: a review on the various techniques

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Received: 28 September 2021 / Accepted: 8 January 2022 / Published online: 27 January 2022  
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## Abstract

Water pollution by recalcitrant compounds is an increasingly important problem due to the continuous introduction of new chemicals into the environment. Choosing appropriate measures and developing successful strategies for eliminating hazardous wastewater contaminants from industrial processes is currently a primary goal. Electroplating industry wastewater involves highly toxic cyanide (CN), heavy metal ions, oils and greases, organic solvents, and the complicated composition of effluents and may also contain biological oxygen demand (BOD), chemical oxygen demand (COD), SS, DS, TS, and turbidity. The availability of these metal ions in electroplating industry wastewater makes the water so toxic and corrosive. Because these heavy metals are harmful to living things, they must be removed to prevent them from being absorbed by plants, animals, and humans. As a result, exposure to electroplating wastewater can induce necrosis and nephritis in humans and lung cancer, digestive system cancer, anemia, hepatitis, and maxillary sinus cancer with prolonged exposure. For the safe discharge of electroplating industry effluents, appropriate wastewater treatment has to be provided. This article examines and assesses new approaches such as coagulation and flocculation, chemical precipitation, ion exchange, membrane filtration, adsorption, electrochemical treatment, and advanced oxidation process (AOP) for treating the electroplating industry wastewater. On the other hand, these physicochemical approaches have significant drawbacks, including a high initial investment and operating cost due to costly chemical reagents, the production of metal complexes sludge that needs additional treatment, and a long recovery process. At the same time, advanced techniques such as electrochemical treatment can remove various kinds of organic and inorganic contaminants such as BOD, COD, and heavy metals. The electrochemical treatment process has several advantages over traditional technologies, including complete removal of persistent organic pollutants, environmental friendliness, ease of integration with other conventional technologies, less sludge production, high separation, and shorter residence time. The effectiveness of the electrochemical treatment process depends on various parameters, including pH, electrode material, operation time, electrode gap, and current density. This review mainly emphasizes the removal of heavy metals and another pollutant such as CN from electroplating discharge. This paper will be helpful in the selection of efficient techniques for treatment based on the quantity and characteristics of the effluent produced.

**Keywords** Adsorption · Electrochemical methods · Electroplating industry effluents · Heavy metals · Membrane filtration · Wastewater treatment

## Introduction

Water's importance in terms of the environment is now widely recognized all around the world. Due to the water contamination and shortage of water, the substantial environmental load is growing, and the loss of natural water supports because its scarcity is becoming more prevalent nowadays (Carolin et al. 2017). Only less than 1% of freshwater is readily accessible for humans, and a majority of the water on the planet is saltwater from seas or oceans, which covers almost 97% of the water (Jin et al. 2016). By

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Responsible Editor: Weiming Zhang

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2025, more than three billion people on the planet will lack access to safe water, with over one-third of this population living in water-stressed regions; by 2050, it is predicted to be two-thirds of the population, according to the WHO (World Health Organization) (Bankole et al. 2019). The rising population has resulted in unplanned habitations giving growth in wastewater discharge without any prior treatment into the rivers/streams, degrading the quality of natural water causing water pollution (Hosseini et al. 2016). Electroplating industries, metallurgical industries, mining operations, power generation facilities, wastewater including heavy metals, and polluted organic pollutants have been released into the atmosphere over the last two decades, particularly in developing countries (Chen et al. 2013). Furthermore, since 1947, industrial electroplating wastewater purification has been viewed as a large-scale protest due to its chemical composition, environmental impacts, and lack of convenient and legal regulations governing its release into the environment (Bankole et al. 2019). In the 1950s, the very first wastewater treatment technology was developed and implemented in industry. Electroplating wastewater contains a significant amount of heavy metal, cyanide-complex, and the complicated composition of effluents and may also include BOD/COD, DS, SS, TS, and turbidity. The electroplating industry wastewater contains about 29% of toxic and hazardous wastes. The concentrations of these toxic metal ions are much higher than the permissible levels. As a result, effluents from the surface finishing and plating industries must be properly treated before being released to avoid causing further environmental damage. Most of them are patents, including the electroplating wastewater and metal recovery system, as reported by Izdebski (1975), Morton (1997), and Adiga (2000). The health effect of exposure to electroplating wastewater, including kidney failure, thyroid dysfunction, sleeplessness, tiredness, rheumatoid arthritis, affects the circulatory system and neural system, causes gastrointestinal mucosa irritation, and leads to lung cancer. The electroplating industry wastewater includes heavy metals such as arsenic (As), cobalt (Co), copper (Cu), chromium (Cr), mercury (Hg), iron (Fe), nickel (Ni), zinc (Zn), and sometimes lead (Pb), cadmium (Cd), and as well as acids, alkalis, and toxic CN (Calero and Bl 2014).

The implementation of an electroplating process incorporates the electrodeposition of a thin metal over another metal. In this process, the electricity passes through an electrolytic bath, dissolving and depositing the metal at the anode and cathode. Pollution is caused by the usage of various chemicals and metals salt. Several series of processes are done during the electroplating process, which involves alkaline cleaning, plating, acid pickling, and rinsing, which create a large amount of untreated wastewater (Babu et al. 2009). This process with waste effluents treatment facilities is carried out in a particular sequence, as shown in Fig. 1. It

is also important to note that waste acid and other coating elements contributed significantly to the treatment process complexity. Electroplating wastewater contains a variety of inorganic and organic species, considering turbidity, dissolved oxygen (DO), COD, BOD, total dissolved solids (TDS), total suspended solids (TSS), phosphate, sulfate, phosphate, CN complexes, and metal ions (Husain et al. 2014; Martin-Lara et al. 2014; Bankole et al. 2017). The primary characteristics of the wastewater generated by the electroplating industry are shown in Table 1.

The main goal of this study is to review the essential opportunities applicable for the removal of electroplating industry contaminants and thus provide a good starting point for future researchers who want to fill research gaps in the field and enhance the advanced wastewater treatment approaches. Although few similar review papers address the treatment of electroplating wastewater involving heavy metals despite its importance as a significant water contaminant, they all seem to be overly generic, including other metal ions or focusing on an individual treatment approach. Electroplating wastewater treatment employs a variety of techniques such as coagulation-flocculation (Xiao et al. 2021), chemical precipitation (Fu et al. 2021), ion-exchange (Zhang et al. 2021), membrane filtration (Njoya et al. 2021), adsorption (Rajivgandhi et al. 2021), and electrochemical treatment (Sahu et al. 2014; Liu et al. 2021; Wang et al. 2021).

## Heavy metals in electroplating industry wastewater

Heavy metals such as Fe, Cu, Cr, Hg, Cd, Ni, Pb, Zn, and many more having a very high concentration are released from the electroplating industry wastewater. Heavy metals have a density of more than five times that of water (Al-saydeh et al. 2017). It is made up of elements having atomic weights ranging from 63.5 to 200.6 (Carolin et al. 2017). Heavy metal levels in the environment are rising, posing a major threat to human health, living resources, and ecosystems. Toxic heavy metals are released from various sources; however, specific industrial sectors are the most polluting. Due to the enormous number of unified firms and their geographical dispersion, the plating or metal finishing industry is significant among these industrial sectors. The process used in electroplating production is the most environmentally adverse industrial process; a considerable amount of wastewater is generated containing heavy metal ions. Because of the severe toxicity of heavy metals, careful consideration has been given. To decrease the risk of toxic substances affecting humans and the environment, wastewater rules were enacted. Table 2 lists the maximum contaminated level (MCL) standards for heavy metals and associated toxicities (Hosseini et al. 2016; Rajoria et al. 2021).

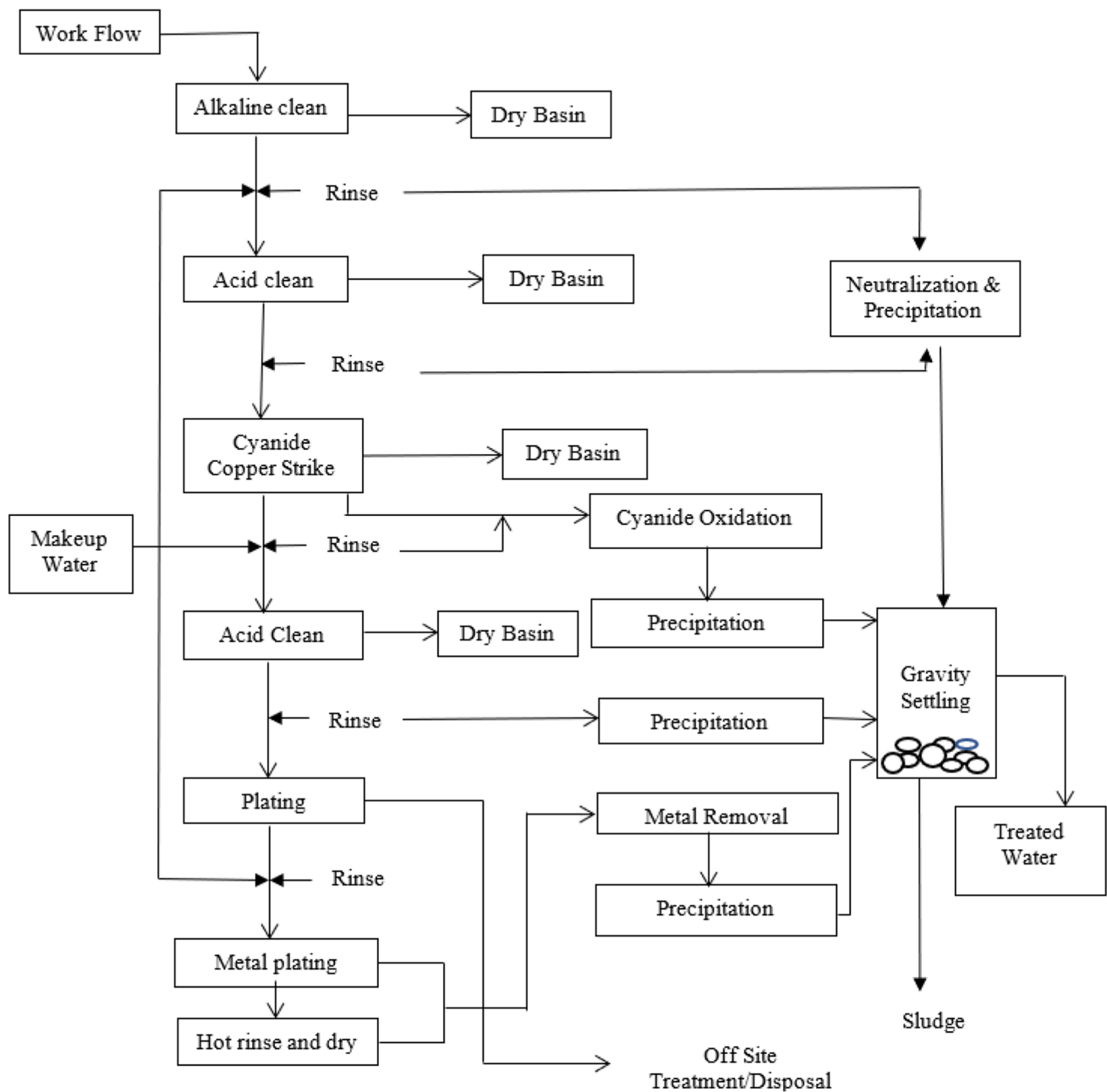


Fig. 1 Typical electroplating process with waste treatment facilities

Non-biodegradable pollutants pose significant health and environmental risk, and secondary procedures cannot be used to remove these wastes. Advanced wastewater treatment processes such as ion-exchange, adsorption, membrane separation, and electrochemical approaches can be employed to remove these resistant pollutants.

### Conventional methods for industrial wastewater treatment

Due to inhibitory properties, pollutants in wastewater can be removed by applying a high removal enforcement

**Table 1** Characteristics of the electroplating wastewater (except turbidity in NTU and color)

Parameter	Range (in mg/L)
pH	2.02–7.6
TDS	1200–6500 ± 80
TSS	175–3800 ± 60
COD	180–3404.4
BOD	1.56–1600 ± 60
Chloride	500–2100 ± 50
Sulfates	400–1450 ± 50
Total alkalinity	100–900 ± 20
Oil and grease	4–8 ± 1
Total residual chlorine	15.58–550
Ni	5.82–1550
Cu	2–2980
Cd	0.03–102
Total Cr	0.19–25,176
Total organic compounds (TOC)	60.95–1278.4
DO	2–4.00
Nitrate	8.92–891.00
Ammonia	50–150
Phosphate	50–278
CN	120–261
Fluoride	100–305
Sulfate	500–1800
Nitrite	1.20–5.70
Calcium	4.2–14.3
Turbidity	34.8–256
Color	Dark yellowish brown, light blue, light green

technology. The appropriate protocols are used for the clearance of water pollutants. In order to minimize pollution emission, water management, and energy

consumption, industries must deal with a variety of issues. As a result, several treatment methods were created to ensure environmental safety, which has grown into an important research topic. Coagulation-flocculation, precipitation, adsorption, membrane filtration, ion exchange, electro-dialysis, electro-flotation, electro-coagulation, electro-oxidation, and advanced oxidation process (AOP) are the most demanding and assuring techniques applicable for reducing the industrial effluent (Yadav et al. 2021). Several patents have been found regarding this type of processes (Kang 2003; Fresnel 2015; Li and Lichun 2017; Chongwu Guo 2020). Figure 2 shows the flow diagram of different wastewater treatment methods. Although all of the above methods can be used to treat wastewater, many aspects must be considered when choosing the best treatment method, including removal performance, efficiency, adaptability, and safety. Most treatment procedures are ineffective and expensive if metal ions concentrations in wastewater are less than 1–100 mg/L (Al-Qodah and Al-Shannag 2017). Fast, clean, cheap, and environmentally friendly approaches should be applied, considered the best removal method. Heavy metals as electroplating effluents are degraded using a series of techniques for proper treatment.

## Coagulation/flocculation technique

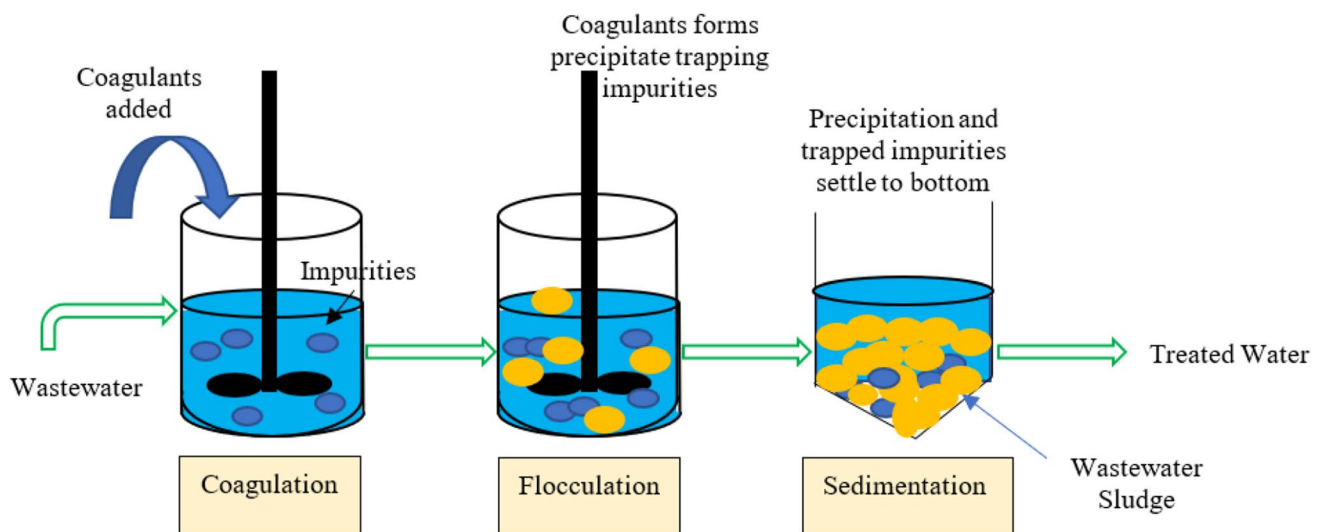
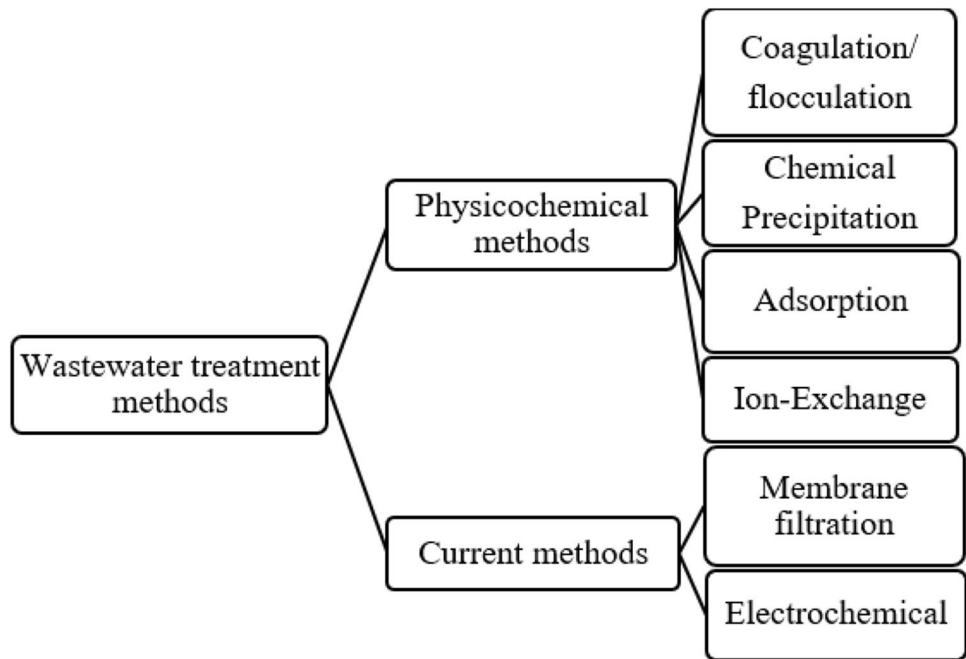
Coagulation is a method in which insoluble or suspended particles are combined into big aggregates to generate coagulants. Coagulants such as aluminum, ferric chloride, ferrous sulfate, and others are often employed in traditional wastewater treatment processes to help in the removal of wastewater particulate contaminants through charge neutralization of particles. Figure 3 shows how coagulation-flocculation has been used to treat drinking water and decontaminate

**Table 2** The MCL standards for the most hazardous heavy metals and their toxicities

Parameter	Toxicities	Maximum value	Maximum effluent discharge standards (mg/L)		
			USEPA	WHO	ISI
As	Diarrhea, cancer, skin lesions	0.1	0.050	0.05	0.05
Cd	Fragile bones, death	0.1	0.01	0.005	0.01
Cr	Skin irritation, blood disorders	0.1	0.05	NA	0.05
Cu	Difficulty breathing, nausea	0.5	0.25	1.0	0.05
Pb	Kidney failure, thyroid dysfunction, insomnia, fatigue	0.2	0.006	0.05	0.10
Hg	Rheumatoid arthritis, affects the circulatory system and neural system	0.01	0.00003	NA	NA
Ni	Dermatitis, chronic asthma, nausea	0.5	0.20	NA	NA
Zn	Depression, neurological signs, lethargy	2	0.80	NA	NA

USEPA United States Environmental Protection Agency, WHO World Health Organization, ISI Indian Standards Institution (ISI)

**Fig. 2** Different treatment methods for wastewater



**Fig. 3** Coagulation and flocculation for wastewater treatment produced

industrial effluents (Yadav et al. 2021). It is also effective for metal ions with concentrations of smaller than 100 ppm or greater than 1000 ppm. This process effectively removes the heavy metal when the pH ranges from 11.0 to 11.5, the same as chemical precipitation. This process cannot entirely remove the effluents in industrial wastewater, and sludge is also produced because of the coagulants used (Chang and Wang 2007). As a result, coagulation or flocculation should be integrated with other wastewater treatment procedures such as precipitation or casual reduction. For example, Bojic et al. (2009) used a micro-alloyed aluminum composite to

investigate an integrated strategy, i.e., a spontaneous reduction-coagulation process to eliminate Zn(II) and Cu(II) metal from wastewater. The flow rate, pH, and metal ions concentration are the operating parameters that were investigated to achieve the higher removal capacity. Tao et al. (2016) studied the effect of Nano coagulants like AgNPs on heavy metal concentration and can reduce the TOC in the wastewater. The advantages of the coagulation-flocculation process include settling suspended materials in a short time interval and superior dewatering properties. In contrast, the disadvantages include sludge generation and high operational

**Table 3** Removal of heavy metal using coagulation–flocculation technique

Heavy metal	Initial conc. (mg/L)	Optimum pH	Dose of coagulant (mg/L)	Coagulants/flocculants	Removal efficiency (%)	Remarks	References
Ni(II), Cu(II), and Zn(II)	60	7	80	Starch acrylamide-acrylic acid (SAA) and Starch acrylamide-2-acrylamido-2-methyl-1-propanesulfonic acid (SAS)	Cu and Zn > 80 Ni > 90	The performance of Starch-graft-P SAS on real wastewater is much higher than that of SAA, implying that the sulfonate groups have a greater potential to capture heavy metal chelates	(Xiao et al. 2021)
Ni	48.8	7	40	CMCTS-g-P(AM-CA)	72.63	A new dual-functional chitosan flocculant CMCTS-g-P(AM-CA) for the flocculation removal of heavy metal was produced using UV-induced graft copolymerization using AM, CMCTS, and ammonium di-thio-carbamate as reaction monomers	(Sun et al. 2020)
Cr and Ni	44.6	6.8	Cr-2.5 Ni-1.0	CAC and CPCTS-g-PAM	Cr-94.6 Ni-99.4	Total Cr removal ratios of 94.7% and 94.6% were reached by CAC and CPCTS-g-P(AM-AMPS), respectively. CAC and CPCTS-g-P(AM-AMPS) also achieved overall total Ni removal rates of 99.3% and 99.4%, respectively The overall Cr and Ni content met environmental criteria after two stages of flocculation, showing that CAC and CPCTS-g-P(AM-AMPS) have a lot of potential in treating wastewater	(Sun et al. 2019)

Table 3 (continued)

Heavy metal	Initial conc. (mg/L)	Optimum pH	Dose of coagulant (mg/L)	Coagulants/flocculants	Removal efficiency (%)	Remarks	References
Pb, Cd, Ni, Zn, Cu, Cr, and Ca	NA	4.5	410	Nonstoichiometric interbiopolyelectrolyte green complexes (NIBPEGCs)	Cu-99.20 Zn-88.83 Cr-98.72 Ni-90.56 Ca-99.00 Cd-79.58 Pb-32.16	Chemical attraction, electrostatic forces, and particle entrapment are all complementary functions of NIBPEGCs made of alginate (AG)/chitosan (Ch) and poly (acrylic acid) (PAA)/(Ch), indicating the possibility of more simple operating units for heavy metal removal Heavy metal removal is more effective with AG/Ch complexes	(Lopez-Maldonado et al. 2017)
Pb(II), Cu(II) and Fe(III)	25	7.1–7.5	NA	Polyvinylamine (PVAm)	Pb(II)-99 Fe(III)-99 Cu(II)-97	The coordination interactions between PVAm and the heavy metals were connected to polymer-enhanced ultrafiltration (PEUF) metal rejection ability	(Huang et al. 2016)
Fe, Cr, Cu	Fe-7.1–7.2 Cr-3.0–3.3 Cu-0.1–0.2	6.13	Coagulant -65.26–170 and flocculant-5.36	Polyaluminium chloride as the coagulant and anionic polyacrylamide as the flocculant	Fe-97.7 Cr-98.7 Cu-78.7	—	(Bakar et al. 2015)

**Table 3** (continued)

Heavy metal	Initial conc. (mg/L)	Optimum pH	Dose of coagulant (mg/L)	Coagulants/flocculants	Removal efficiency (%)	Remarks	References
Pb, Zn, Fe	25–45	Alum-6.2–7.8, MgCl <sub>2</sub> -8.7–10.9, PACl-8.0–9.3	NA	Alum, magnesium chloride (MgCl <sub>2</sub> ), and polyaluminium chloride (PACl)	< 99	The inclusion of primary coagulant decreased the flocs settling time, which was determined to be MgCl <sub>2</sub> > PACl > alum. Adding 2.0 mL of coagulant aid to alum and PACl-treated solutions can result in less than 100 s of flocs settling time, whereas MgCl <sub>2</sub> treatment requires a minimum of 5.0 mL of coagulant aid	(Pang et al. 2011)
Cu(II)	20	6	100–150	Tanfloc	90	Among the coagulants studied, PACl was the most effective	(Heredia and Martín 2009)
Zn(II)	20	7	100–150	Tanfloc	75	Tanfloc has been shown to be a highly efficient flocculant in the elimination of heavy metals from surface water	(Heredia and Martín 2009)
Ni(II)	20	8	100–150	Tanfloc	70	Compared to chemical precipitation and the classic coagulation–flocculation procedure, Tanfloc has various advantages. Some of them are its natural origin, its relatively simple manufacture by chemical alteration of tannins, and the fact that pH regulation is not as difficult as it is for Al and Fe salts	(Heredia and Martín 2009)



Table 3 (continued)

Heavy metal	Initial conc. (mg/L)	Optimum pH	Dose of coagulant (mg/L)	Coagulants/flocculants	Removal efficiency (%)	Remarks	References
Ni(II), Cu(II), Cr(II)	Ni-13.4 Cu-113.6 Cr-429	3	160	Polyethyleneimine-sodium xanthogenate (PEX)	95	PEX is capable of removing turbidity as well as heavy metal ions According to turbidity measurements, the pH of its iso-electric point was 3.0. The iso-electric point determination and PEX's coagulation characteristic were in good agreement	(Chang and Wang 2007)
Cu(II)	20	10–11.5	25	Poly-ferric sulfate	99.6	The trapping agent is sodium diethyldithiocarbamate (DDTC), while the flocculants are poly-ferric sulfate and polyacrylamide	(Li et al. 2003)
Cu(II)	20	10–11.5	5	Poly-acryl amide	95	Furthermore, at a pH of 10, the effects of DDTC on Cu trapping are more effective than those of diethylammonium diethyldithiocarbamate (DDC) and ammonium pyrrolidinedithiocarbamate (APDC)	(Li et al. 2003)

costs due to chemical requirements. Table 3 shows the outcomes of specific research projects that used coagulation-flocculation to remove effluents from wastewater.

## Chemical precipitation technique

Chemical methods have become widely used in various processes in recent decades of electroplating industry development due to their mature techniques and low investment. Chen et al. (2009a) show the general flow of chemical precipitation methods in Fig. 4. It is an appropriate method for treating electroplating industry wastewater, including cyanide, heavy metals, etc. Although chemical treatment of electroplating wastewater is fundamentally an ultimate treatment strategy, it can only minimize the quantity of treatment discharged and cannot completely heal the problem (Lu and Wu 2020). In this process, chemicals react with heavy metals in wastewater, leading to the formation of insoluble precipitates. In the modern electroplating industry, the chemical precipitation of heavy metals using lime, sulfide, and caustic soda is the most extensively used treatment process, which occupied pH arrangement to necessary conditions to minimize metal ions solubility in the effluent (Ku and Jung 2001).

Hydroxide precipitation and sulfide precipitation are two types of processes used in the chemical precipitation technique. Cr, Cu, Zn, Cd, and Mn are easily removed by applying the chemical precipitation technique (Bilal et al. 2013). Most of them are patents, including the removal of the Cu complex reported by Zhou (2013). The chemical precipitation method has advantages like a simple operation, low-cost precipitant agents, and minimal initial investment due to their being easily accessible. At the same time, the disadvantages include that it generates a huge quantity of sludge that has to be treated further to extract metals, ineffective with the low concentration of metal ions, and sludge clearing issues, all of which have long-term negative environmental consequences (Barakat 2011; Fu and Wang 2011). Table 4

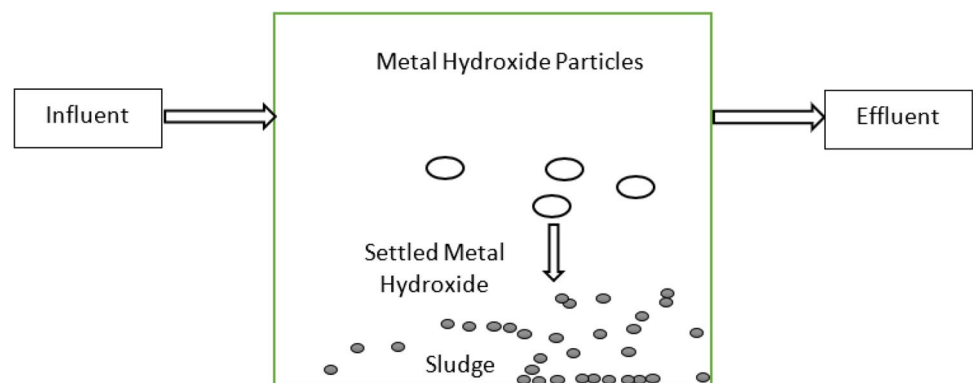
shows the outcomes of specific research work that used chemical precipitation to remove effluents from wastewater.

## Ion-exchange technique

Ion-exchange is a wastewater treatment separation process that can eliminate a large amount of metal ions. This technique replaces the ions with another for wastewater treatment, resulting in high-quality treated water that may be reused. As a response, ion-exchange resins of various sorts have been utilized to treat wastewater containing mixed metal ions as well as inorganic and organic contaminants (Bisht and Agarwal 2017). Synthetic resins are the most extensively approved of all the materials used in ion-exchange techniques. This resin can eliminate almost all heavy metals from a solution. Temperature, pH, initial concentration, and retention time all influence the uptake of heavy metal ions by ion-exchange resins (Gode and Pehlivan 2006). Several patents for this method have been identified (Etzel 1980; Katoh 1985). In 1995, ion exchange resin (MIEX) was used to remove natural organic materials; this resin is regarded as the first ion exchange resin (Ambashta and Sillanpaa 2010). Figure 5 shows the cation exchange resin in column ion-exchange tests to remove metal ions (Yadav et al. 2021).

Cavaco et al. (2007) tested the performance of ion exchange resins in the removal of Cr (III) from untreated wastewater. Overall, the chelating resin (Diaion CR11) appears promising for electroplating effluent treatment. According to the findings, Zewail and Yousef (2015) developed a batch conical air spouted tank for Ni and Pb removal from wastewater utilizing strong cation exchange resins (Ambserjet 1200 Na). They also look at how other factors like contact time, superficial air velocity, and the initial concentration of heavy metal ions affect the proportion of heavy metal removed. They were able to remove 99% of Pb and 98% of Ni, respectively, under optimal conditions. Alyüz and Veli (2009) examined the elimination of Ni and Zn from aqueous solutions using

**Fig. 4** Electroplating wastewater chemical precipitation treatment method



**Table 4** Removal of heavy metal using chemical precipitation technique

Heavy metal	Precipitant	Initial conc. (mg/L)	Contact times	pH	Removal efficiency (%)	Remarks	References
Ni	Ca(OH) <sub>2</sub>	36.53	NA	7.0±0.2	90	The direct treatment of real electroplating effluent with (Lemna minor) LM400 showed a limited effect, but discharge criteria might be met when combined with biochar adsorption and pre-precipitation with Ca(OH) <sub>2</sub>	(Yan et al. 2020)
Cr	Ca(OH) <sub>2</sub> and NaOH	122	NA	9	98.2	To precipitate Cr(III) as hydroxides, precipitating agents such as Ca(OH) <sub>2</sub> , (NaOH), and a mixture of the two was utilized Ca(OH) <sub>2</sub> + NaOH is the best combination since it has the highest removal efficiency	(Bharti 2020)
Cu(II), Zn(II) and Pb(II)	Ca(OH) <sub>2</sub> , (Na <sub>2</sub> CO <sub>3</sub> ), (Na <sub>2</sub> S)	100	NA	9	Zn-99.99 Cu-99.99 Pb-99.75	Carbonate precipitation was a successful treatment option to hydroxide precipitation, and being able to operate at a lower pH range, often around pH 9. Soda ash can be applied to remove dissolved metal ions from wastewaters (Na <sub>2</sub> CO <sub>3</sub> ) With a removal rate of > 99.75%, sulfide precipitation by adding Na <sub>2</sub> S was the most viable and effective approach for eliminating heavy metals from aqueous solutions	(Chen et al. 2018)
Cr(VI), Ni(II), Pb(II), Cu(II), Zn(II)	Biochar (BC) and iron sulfide (FeS)	NA	3 days	8.3	Cr-59.6, Cu-100, Ni-63.8, Pb-73.5, Zn-90.5	Both BC and FeS ES treatment approaches were claimed to be low-cost, simple, environmentally friendly, and time-saving. FeS has a stronger ability for heavy metal immobilization than BC	(Lyu et al. 2016)

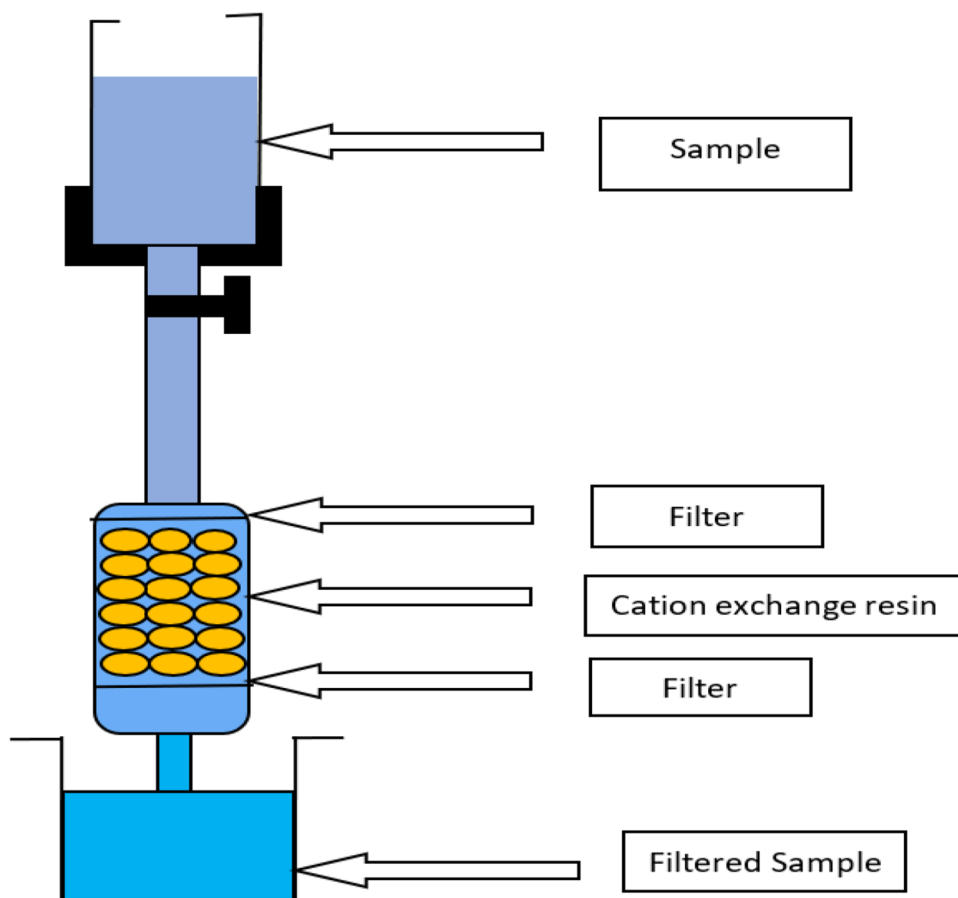
**Table 4** (continued)

Heavy metal	Precipitant	Initial conc. (mg/L)	Contact times	pH	Removal efficiency (%)	Remarks	References
Cr	NaOH + Ca(OH) <sub>2</sub>	1000	NA	7	99.7	The best precipitating agent for Cr removal is a mixture of NaOH + Ca(OH) <sub>2</sub>	(Ramakrishnaiah 2012)
Zn	Lime (CaO)	32	NA	10	99	A combination electro-Fenton followed by a lime precipitation approach is presented as a successful treatment of industrial wastewater with high COD and Zn concentrations	(Ghosh et al. 2011)
Zn(II)	NA	5–90	NA	8.7 to 9.6	99	As the metal concentration raised, the effectiveness of heavy metal removal by hydroxide precipitation increased. The hydroxide precipitation and coagulation–flocculation approach were utilized to treat wastewater containing Zn, Cu, and Fe	(Pang et al. 2009)
Cu(II)	NA	3–90	NA	8.1 to 11	99		(Pang et al. 2009)
Fe(III)	NA	5–45	NA	6.2 to 7.1	99		(Pang et al. 2009)
Cu, Zn, Cr, Pb	Lime	100	60 min	7–11	99.37–99.69	Heavy metals precipitation with calcium oxide in the presence of fly ash has been demonstrated to lower the concentration of soluble heavy metal in solution	(Chen et al. 2009a)
Hg(II)	1,3-Benzenediamidoethanethiolate (BDET <sup>2-</sup> )	65.6 (ppb)	NA	4.7 and 6.4	> 99.9	While BDET is currently more expensive per gram than commercial reagents, far less BDET is needed to achieve higher levels of Hg elimination	(Blue et al. 2008)

Table 4 (continued)

Heavy metal	Precipitant	Initial conc. (mg/L)	Contact times	pH	Removal efficiency (%)	Remarks	References
Cr(III)	CaO and MgO	5363	NA	8.0	> 99	CaO and MgO precipitate settled significantly faster than $\text{Na}^+$ precipitates due to the bridging capability of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ . The most common process for recycling Cr(III) recycle is NaOH precipitation, which is greatly restricted by the poor sedimentation of the sludge formed	(Guo et al. 2006)
Ni(II)	NA	51.6	< 2 h	10.5	85	The combination of ion-exchange and precipitation techniques resulted in a greater reduction in Ni concentrations (from 94.2 to 98.3%)	(Papadopoulos et al. 2004)
Fe	1,3-Benzenediamidoethanethiol dianion (BDET)	194	NA	4.5	> 90	BDET can be used as an additive to minimize metal concentrations because of the remarkable stability of the precipitates under oxidative and pH conditions	(Matlock et al. 2002)

**Fig. 5** Column ion exchange used for heavy metal removal



Dowex HCR S/S cation exchange resin. Dowex HCR S/S type resins can reduce residual heavy metal concentrations below discharge limits because they are sodium-based and have excellent cation exchange capabilities. The influences of pH, resin dosage, and contact time on the removal process were investigated using batch shaking adsorption tests. The most efficient elimination of Ni and Zn was found to be at pH 4 and 6, respectively. Ni and Zn adsorb to equilibrium in 90 min and 120 min, respectively. They found that under ideal conditions, Ni and Zn were removed from aqueous solutions at a rate of more than 98%. Besides the great use of the ion-exchange process, it also raises the operational cost, and on a large scale, it cannot be appropriate for wastewater treatment. The limitations of this method are high resin cost, slow operation rate, regenerations of resins, high capital, and operational cost. Ion exchange is also a nonselective mechanism that is extremely sensitive to the pH of the solution (Barakat 2011). The results from some research work using the ion-exchange method to remove heavy metals from wastewater are shown in Table 5.

### Membrane filtration technique

Membrane filtration is a pressure-driven process of separation that has been used in wastewater treatment. Membrane filtration has several advantages over other traditional techniques, including high separation performance, energy savings, the ability to scale up quickly, high efficiency in recovering heavy metal ions, and being environmentally friendly (Zhu et al. 2014). Besides some advantages, it also has some disadvantages, such as the operational cost is high due to membrane fouling, costly membrane sheets for high removal of heavy metals, and low permeate flux (Malaviya 2011). It depends upon the different variety of membrane various membrane filtration techniques were employed. Heavy metals can be removed via membrane filtering techniques like ultra-filtration (UF), reverse osmosis (RO), and nano-filtration (NF), which are all dependent on particle size retention. On the basis of pore size (0.05 to 0.1 microns) and molecular weight of the separating compounds (1000–100,000 Da), UF uses a permeable

**Table 5** Heavy metal removal using the ion-exchange method

Heavy metal	Resin	Operating style	Initial conc. (mg/L)	Optimum pH	Removal efficiency (%)	Remarks	References
Pd	Novel mesoporous ion-exchange resin (SiAcyl)	Batch	NA	1.95	100	SiAcyl resin demonstrated good stability, reusability, and cost-effectiveness compared to various existing commercial resins for possible usage in industrial applications	(Zhang et al. 2021)
Cr, Cu	Strongly acid sulfonated polystyrene CER cation exchange resin	NA	Cu-0.056–0.137 Cr-0.442–1.111	7.01–7.78	Cu-91.25 Cr-95.9	To remove refractory organics and heavy metals, in situ ion-exchange electrocatalysis biological coupling (i-IEEBC) is a cost-effective and readily accessible approach. COD, TOC, Cr, and Cu ions are removed at a significantly faster rate by i-IEEBC than by BAF, with values of $87.23 \pm 1.00\%$ , $80.42 \pm 0.59\%$ , $91.25 \pm 4.53\%$ , and $95.97 \pm 3.00\%$ , respectively	(Feng et al. 2019)
Cr	Strong-base silica-supported pyridine resin, SiPyR-N4	Batch	100	4	99.3	The D201 resin's Cr(VI) treatment capability was less than half that of SiPyR-N4 under the same conditions, while the IRA-400 resin was totally disabled. These results demonstrated that SiPyR-N4 ion-exchange had a high selectivity for Cr(VI) and even excellent adsorbability in acidic conditions	(Ye et al. 2019)
Ni(II)	Cation-exchange resin	Batch	100	5–7	95.6	Pilot-scale fixed-bed resin adsorption was used to recover Ni from actual nickel plating effluent. Electrodeposition was used to convert the concentrated Ni ions in the regenerated solution to nickel sheet	(Li et al. 2019)

**Table 5** (continued)

Heavy metal	Resin	Operating style	Initial conc. (mg/L)	Optimum pH	Removal efficiency (%)	Remarks	References
Cu(II)	Polyethyleneimine modified ion-exchange resin (PMR) and unmodified resin (UMR)	Batch	200	5–6	99.9	For removing Cu(II) ions from SEPRW, the PMR was shown to be a better sorbent than the UMR. The following was the order of the most impressive adsorption capacity (Q <sub>max</sub> ): PMR > UMR	(Revathi et al. 2016)
Ni, Pb	Amberjet 1,200 Na	Batch	800, 1000, 1250	NA	99	—	(Zewail and Yousef 2015)
Cu	INDION225H	NA	50–150	6.3–6.5	NA	Because of its high density and smooth surface, INDION225H is a superior choice for expanded bed adsorption	(Thakare and Jana 2015)
Cu	Strong acid cation-exchange Dowex	Batch	100	3.2±0.1	NA	Hybrid ion-exchange electro dialysis, also known as electrode ionization (IXED), is a method that combines traditional ion exchange (IX) with electro dialysis (ED) to improve mass transfer and the limiting current density, allowing for a more successful treatment process	(Mahmoud and Hoadley 2012)
Ni, Zn	Dowex HCR S/S	Batch	100	Ni-6 Zn-4	99	Because of their significant cation exchange capabilities, Dowex HCR S/S type resins reduce residual heavy metal concentrations. They are also generally available because as they are commercially produced	(Alyüz and Veli 2009)
Cr, Cu, Fe, Mg, Ca	Diaion CR11 and Amberlite IRC86	NA	Cr-729.0 Cu-5.9 Fe-15.6 Mg-9.3 Ca-68.9	2.6	NA	At 50 °C, the chelating resin (Diaion CR11) in the Na <sup>+</sup> form showed a greater sorption capacity, suggesting that it could be used to remediate effluent from the electroplating industry	(Cavaco et al. 2007)

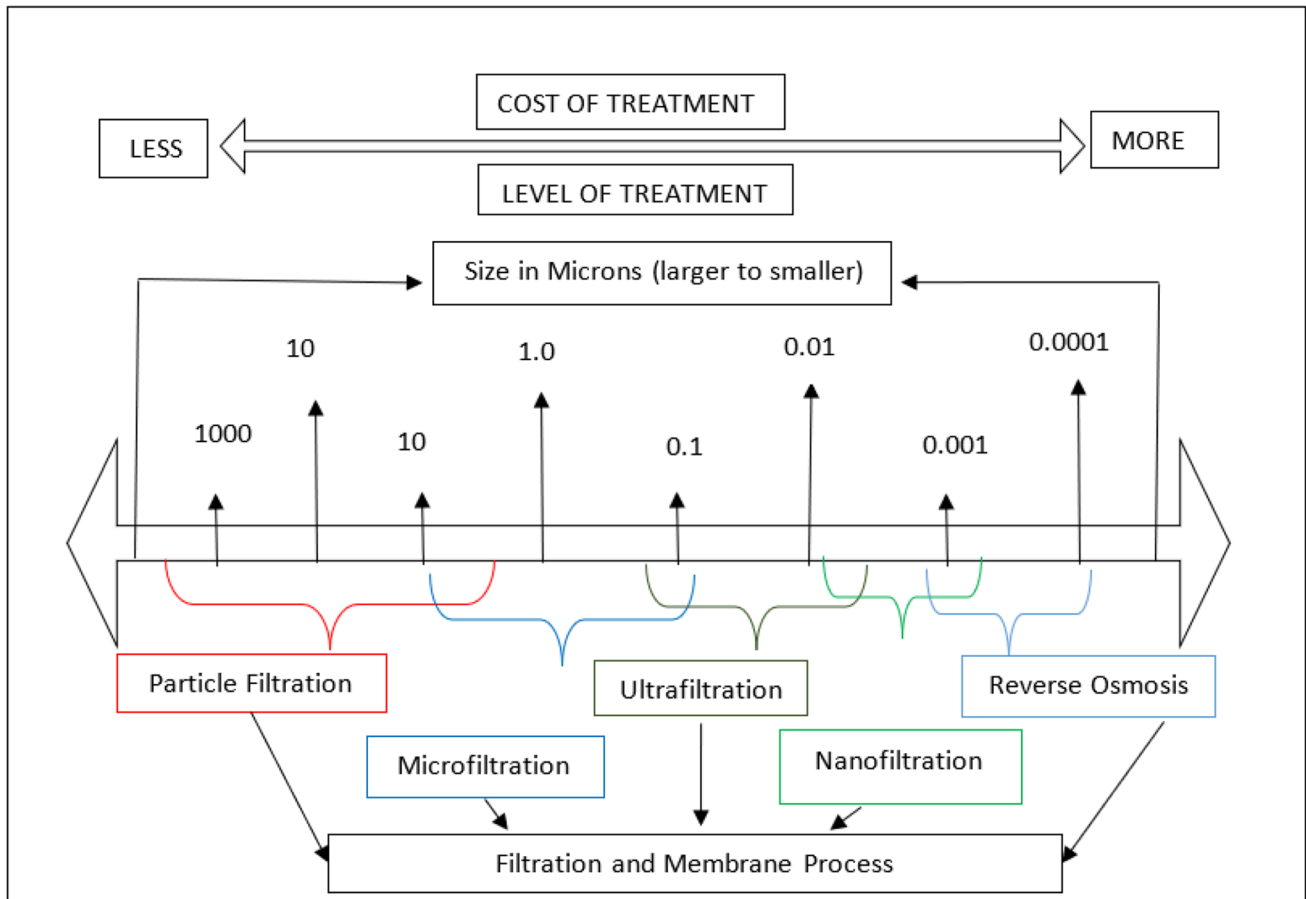


Table 5 (continued)

Heavy metal	Resin	Operating style	Initial conc. (mg/L)	Optimum pH	Removal efficiency (%)	Remarks	References
Cr(VI)	Solvent impregnated resins	Batch	NA	5.0	99.5	The benefits of SIR (solvent impregnated resins) include a large selection of solvent extraction reagents, the flexibility of preparation, and the ability to run continuously	(Kabay et al. 2003)
Zn(II)	Acidic resin with sulfonic acid functionality and	Continuous	NA	NA	100	—	(Idrisb et al. 1996)
Cr(VI)	Basic resin with trimethylbenzyl-ammonium	Continuous	NA	NA	100	—	(Idrisb et al. 1996)

membrane to separate heavy metals, macromolecules, and suspended particles from inorganic solution. Water can pass through the membrane in RO, a pressure-driven membrane process, while heavy metals are retained. Due to the progressively stringent environmental legislation, RO has been designed with a membrane pore size in the range of (0.0005 to 0.001 microns). NF membrane has tiny pores and membrane surface charge, which rejected the bigger neutral solutes or salts and permitted to pass the charged solutes smaller than the membrane pores. Figure 6 illustrates the various membrane technologies and their ability to remove multiple species, including heavy metal ions. Basic parameters such as pH, temperature, pressure, feed concentration, membrane configuration, and size affect membrane performance (Saeid et al. 2016).

Juang and Shiau (2000) published some major research on removing Cu(II), Co(II), Ni(II), and Zn(II) ions from aqueous solutions applying chitosan enhanced membrane filtration. The ultra-filters were made using amicon-generated cellulose YM10 and YM30. With an initial Cu(II) concentration of 79 mg/L and Zn(II) concentration of 81 mg/L and pH ranging from 8.5 to 9.5, Cu (II) ions were removed 100%, and Zn(II) ions were removed 95%. Due to its greater coordination with chitosan, Cu (II) removal is more competent than other metals. Their studies revealed that chitosan increased metal removal by 6–10 times as compared to using a membrane alone. Mohammadi et al. (2009) investigated the effectiveness of RO technology in removing Cr from synthetic wastewater samples prepared in the same way as electroplating industrial effluent. To measure the efficiency of Cr removal, researchers used a pH 6 to 7, an applied pressure of 200 psi, a temperature of around 25°C, and a feed Cr concentration of 10 mg/L. The efficiency of Cr removal was as high as 99% under the optimized conditions. Qin et al. (2002) examined the RO technique to treat spent rinse water from metal plating to meet the standards for reuse as alkaline rinse water. Due to proper ultrafiltration (UF) coupling with RO membrane, appropriate UF pre-treatment might reduce RO membrane fouling and boost RO membrane flux by 30–50%. At permeate conductivities below 45S/cm, Ni, nitrate, and TOC concentrations were 0.01, 2.1, and 3.0 ppm, respectively, with conductivity rejections of over 97%, 99.8%, 95%, and 87%. However, Cimen (2015) employed reverse osmosis with AG, SWHR, SG, and SE membranes to study chromium removal from wastewater. The amount of chromium rejected was determined by the membrane type, operating pressure, pH, and feed water concentration. The membrane's rejection capacity increased in the following order: AG > SWHR > SG > SE. Low Cr (VI) concentrations of 50–100 mg/L produced good results. Using the AG membrane, 91% removal efficiency and permeate flux were achieved. pH 3, 100 mg/L concentration, and 20 bar pressure were shown to be the optimal conditions



**Fig. 6** The range of application of membrane processes for the separation of metal ions

for chromium rejection from wastewater utilizing AG membrane. Wei et al. (2013) studied the removal of heavy metals from real electroplating effluent using thin-film composite NF hollow-fiber membranes. The concentrations of Cr, Cu, and Ni ions in the retentate were 5.72, 5.66, and 5.63 times greater, respectively, than their original feed values. Under pressure (0.4 MPa) and pH 2.31, the removal efficiency for Cr, Cu, and Ni ions was 95.76%, 95.33%, and 94.99%, respectively. Table 6 shows that, compared to UF and NF as membrane filtration, RO is more effective in removing heavy metals from wastewater.

## Adsorption technique

Adsorption is a method for removing heavy metals from wastewater that is frequently employed. Adsorption is a mass transfer process in which a material is transported from the liquid phase to a solid's surface and is bound by physical and chemical interactions (Babel 2015). This procedure forms an adsorbate coating on the adsorbents' surfaces. The adsorbents have a high adsorption capacity and a large interfacial

area. Desorption can be used to reverse the adsorption process and recreate the adsorbents. Adsorbents can be made from natural materials, agricultural waste, and industrial by-products. The most effective adsorbents in the adsorption process are activated carbon (AC), carbon nanotubes (CNT), and low-cost adsorbents, including clay, biomass, peat, and so on. All of these adsorbents are reviewed further below. This technique adsorption has significant economic and environmental benefits, including cheap operating costs, easy availability, profitability, and high productivity Agustiono et al. (2006) analyzed several papers on the removal of heavy metals Cr(III), Cu(II), Cd(II), Cr (VI), Ni(II), and Zn(II) from electroplating wastewater using a variety of low-cost adsorbents made from natural materials, agricultural residues, or industrial by-products.

Furthermore, Alslaibi et al. (2013) employed micro-waved olive stone activated carbon to extract Cd from an aqueous solution. The interaction and relationship between operating factors (i.e., radiation power, radiation time, and impregnation ratio) were investigated using central composite design (CCD) and response surface methodology (RSM). When the radiation power and impregnation ratios

**Table 6** Membrane filtration techniques for heavy metal removal

Type of application	Heavy metal	Type of membrane	Initial conc. (mg/L)	Optimum pH	Pressure	Removal system	Removal efficiency (%)	Remarks	References
NF	Cu, As, Cr	P-60S and P-60S-EDTA with polyethylenimine (PEI) and EDTA-modified PEI	NA	7 ± 0.05	8 bar	NA	Cu-99.82 As-96.75 Cr-97.22	P-60S-EDTA membrane's excellent stability in continuous operation for 36 h in ideal and actual water environments suggests that it could be used in real-world heavy metal contaminated wastewater treatment	(Roy et al. 2020)
UF	Cu, Zn	Polyacrylate sodium (PAAS)	Zn-209 ± 3 Cu-23.6 ± 1	7	0.01 MPa	NA	99	–	(Tang and Qiu 2019)
NF	Ni(II), Zn(II), and Ca(II)	Anion exchange (AEM, Ultrex AMI-7001 and cation exchange (CEM, Ultrex CMI-7000)	Ca(II)-608 ± 17 Ni(II)-1032 ± 35 Zn(II)-11 ± 2	5.6 ± 0.3	NA	NA	Ni(II)-94 Zn(II)-82 Ca(II)-91	The Fenton process with the MEDCC (microbial electrolysis desalination and chemical production cell) eliminated significantly more COD from the NF concentrate than the method without the MEDCC	(Lan et al. 2019)
RO	Cr, Cu, Zn, Ni	Ultra-low-pressure aromatic polyamide	300	4 to 7	1 to 4 bar	NA	Cr-48.5 Cu-50.68 Zn-54.56 Ni-46.18	–	(Al-alawy 2017)
NF	Cr, Cu, Zn, Ni	Polyamide thin film composite	300	4 to 7	1 to 4 bar	NA	Cr-71.75 Cr-75.62 Zn-80.87 Ni-60.06	–	(Al-alawy 2017)

**Table 6** (continued)

Type of applica-tion	Heavy metal	Type of membrane	Initial conc. (mg/L)	Optimum pH	Pressure	Removal system	Removal efficiency (%)	Remarks	References
UF	Pb(II), Cu(II), and Fe(III)	Polyvinylamine (PVAm)	25	7.1–7.5	200 kPa	NA	Pb(II)-99 Cu(II)-97 Fe(III)-99	The PVAm–metal complexes also precipitated from the solution at high metal concentrations when divalent sulfate anions were present. PVAm might thus be employed as a flocculant in the flocculation process to remove metal	(Huang et al. 2016)
NF	Pb(II)	AFC 80	NA	5.8	25 bar	Both	> 98	NF has several advantages over other membrane technologies, including greater energy efficiency, lower operating pressure, stronger divalent ion rejection, and lower monovalent ion rejection compared to RO	(Gherasim and Mikulasek 2014)
NF	Cd, Ni	NA	5	5.0±0	20 × 105 N/m <sup>2</sup>	NA	CdSO <sub>4</sub> -97.26 NiSO <sub>4</sub> -98.90 CdCl <sub>2</sub> -80.57 NiCl <sub>2</sub> -85.27	The rejections of Cd and Ni ions in a CdCl <sub>2</sub> –NiCl <sub>2</sub> –pH changes highly influence the water system	(Chaudhari and Murthy 2010)

Table 6 (continued)

Type of application	Heavy metal	Type of membrane	Initial conc. (mg/L)	Optimum pH	Pressure	Removal system	Removal efficiency (%)	Remarks	References
NF	Cr(VI)	Composite polyamide membrane	1000	2–11	5 bar	Continuous	84–99.7	For this study, two membranes were used: one with a high rejection index (NFI) and the other with a low rejection index (LRI) (NFII). The % rejection of chromium increased as the pH of the feed solution increased	(Muthukrishnan and Guha 2008)
NF	Cr(VI)	Composite polyamide membrane	1000	2–11	8 bar	Continuous	47–94.5		(Muthukrishnan and Guha 2008)
RO	Cu(II), Ni(II)	Thin-film composite spiral wound	500	5	3 atm	NA	99.5	Cu <sup>2+</sup> was removed from the model solutions more than Ni <sup>2+</sup> due to its greater ionic size Using Na <sub>2</sub> EDTA, the rejection of Cu <sup>2+</sup> and Ni <sup>2+</sup> from model solutions increased to 99.5%	(Mohsen-Nia et al. 2007)
RO	Cu(II)	Polyamide	200	4–11	7 bar	NA	Cu (II)-98 Cd (II)-99	Heavy metals were removed efficiently using the RO process (99.4%) and lowering the ion concentration from 500 ppm to around 3 ppm, whereas the average removal effectiveness of NF was 97%	(Abu and Moussab 2004)

**Table 6** (continued)

Type of application	Heavy metal	Type of membrane	Initial conc. (mg/L)	Optimum pH	Pressure	Removal system	Removal efficiency (%)	Remarks	References
NF	Ni(II)	NTR-7250	2000	3–7	2.9 bar	NA	94	In single-salt system experiments, NF eliminated more Ni in NiSO <sub>4</sub> solution than that from NiCl <sub>2</sub> solution	(Ahn et al. 1999)

are 565 W and 1.87, respectively, they found that 7.0 min of contact time is required to achieve 96.25% Cd(II) elimination and 86.05% olive stone activated carbon (OSAC) yield. For treating heavy metal-contaminated water, Guo et al. (2010) employed poultry litter as a precursor material in the manufacture of AC. They accepted that commercial activated carbons made from bituminous coal and coconut shell had much higher adsorption affinity and capacity for most heavy elements than poultry litter-based activated carbon. They also noticed that nutrient and metal ion emissions from litter-derived carbon did not constitute a risk of secondary water contamination. In a study conducted, Kongsuwan et al. (2009) demonstrated the potential of employing AC extracted from eucalyptus bark and processed using the phosphoric acid activation method to manage heavy metals in low-strength wastewater. After that, the AC was used to sorption of Cu(II) and Pb(II) ions. The greatest sorption capacities for Cu(II) and Pb(II) were 0.45 and 0.53 mmol/g, respectively, at the ideal pH for sorption of 5. Accordingly to Jiang et al. (2010), heavy metal ions such as Cd(II), Pb(II), Cu(II), and Ni(II) may be eliminated from real wastewater using kaolinite clay from Longyan, China. The adsorption of metal ions onto kaolinite clay is influenced by a number of factors, but the solution pH has a substantial impact. The selectivity sequence for adsorption of these metals was Pb(I I) > Cd(II) > Ni(II) > Cu(II), while desorption of Cd(II) and Cu(II) was easier than Pb(II) and Ni(II). The absorption is rapid, with maximum adsorption taking place in less than 30 min. The amount of Pb(II) in the water was lowered by this clay from 160.00 to 8.00 mg/L. A variety of sorbents have already been investigated by a number of researchers. Some of the potential low-cost sorbents include bark/tannin-rich materials, lignin, chitin/chitosan, dead biomass, seaweed/algae/alginate, xanthate, zeolite, clay, ash, modified wool, peat moss, leaf mold, iron-oxide-coated sand, bone gelatin beads, and modified cotton. The results of altering the pH, contact time, initial metal concentration, adsorbent, and dosage as adsorption parameters are shown in Table 7.

## Electrochemical techniques

The electrochemical technique was initially used to treat wastewater in England in 1889 (Wang et al. 2007b). These electrochemical approaches proved to be a great alternative to the standard physicochemical electroplating wastewater treatment techniques (Chen et al. 2009b; Rodríguez R et al. 2009). Electrochemical treatment, in comparison, is a promising approach that provides some benefits over other methods for remediation of recalcitrant pollutants, such as no requirement of further chemical reagents, low-cost operation, high selectivity at ambient temperature, and pressure, and vigorous achievement and eco-friendly.

**Table 7** Removal of heavy metals using various adsorption techniques

Adsorbent	Heavy metal	Modifying agent	Initial conc. (mg/L)	Contact time (h)	Dose adsorbent (g/L)	Adsorption capacity (mg/g)	Initial pH	Adsorption system	Removal efficiency (%)	Remarks	References
Biochar (U AJS)	Zn(II) and Pb(II)	NA	Zn-20	1	Zn(II)-2.2 Pb(II)-3.4 (g/L)	Zn(II)-221.1 Pb(II)-119.8	5.1	NA	NA	Ultrasonic-assisted jujube seeds ions (UAJS) yielded Langmuir capacities of 221.1 mg/g for Zn(II) ions and 119.8 mg/g for Pb(II). As a result, as compared to raw jujube seeds (RJS), the UAJS has a greater capacity	(Gayathri et al. 2021)
Biochar	Ni	NA	36.53	NA	2.0 and 3.0 g/L	41.68	7.0±0.2	Batch	90	The direct treatment of real electroplating effluent with (Lemma minor) LM400 showed a limited effect, but discharge criteria might be met when combined with biochar adsorption and pre-precipitation with Ca(OH) <sub>2</sub>	(Yan et al. 2020)

Table 7 (continued)

Adsorbent	Heavy metal	Modifying agent	Initial conc. (mg/L)	Contact time (h)	Dose adsorbent	Adsorption capacity (mg/g)	Initial pH	Adsorption system	Removal efficiency (%)	Remarks	References
Rice husk	Pb(II), Cd(II), Ni(II)	NA	4,957, 1,962, 2,626 mg/L Cd(II), Ni(II), Pb(II)	0.5	NA	Pb(II)-295.20 Cd(II)-151.51 Ni(II)-72.80	5.5	Batch	Pb(II)-99.92 Cd(II)-99.98 Ni(II)-96.38	Rice Husk (RHMWX) was effectively prepared by microwave irradiation and had several distinct advantages, including low cost, quick preparation, and strong absorptivity	(Qu et al. 2020)
Activate carbon	Cr, Cu Zn	NA	50	2.66	5 and 4 g/L	NA	4	NA	Cr(VI)-97 Cu-97.4 Zn-96	TiO <sub>2</sub> ; AC has a high adsorption capacity and can be used in the treatment of heavy metals. The adsorption percentages of these ions increased significantly as the adsorbent dosage was increased	(Ayub et al. 2020)



Table 7 (continued)

Adsorbent	Heavy metal	Modifying agent	Initial conc. (mg/L)	Contact time (h)	Dose adsorbent	Adsorption capacity (mg/g)	Initial pH	Adsorption system	Removal efficiency (%)	Remarks	References
RES and calcined electroplating sludge (CES)	Ni	NA	547.2	24	4.0 g/L	CES-163.6 RES-210.9	6.52	NA	NA	The raw electroplating sludge (RES) had a substantially better adsorption capacity for Ni <sup>2+</sup> in real nickel-containing wastewater treatment than commonly used adsorbents such as activated carbon, various cation-exchange, and chelating resins	(Peng et al. 2020a)
CES	Ni(II)-citrate	NA	283 ± 3.8	0.83	1.5 g/L	183.09	7.63 ± 0.15	NA	87	In the novel calcined electroplating sludge (CES)/H <sub>2</sub> O <sub>2</sub> system, the resulting CES was an effective catalyst and adsorbent for treating real electroplating effluent containing Ni(II)-citrate	(Peng et al. 2020b)

Table 7 (continued)

Adsorbent	Heavy metal	Modifying agent	Initial conc. (mg/L)	Contact time (h)	Dose adsorbent	Adsorption capacity (mg/g)	Initial pH	Adsorption system	Removal efficiency (%)	Remarks	References
Activate carbon prepared from grape	Cd(II) Pb(II)	NA	NA	NA	NA	NA	5.5 and 6	NA	98	Despite having the smallest BET area, grape pomace activated carbon outperformed the other materials	(Sardella et al. 2015)
Olive stone	Cr(VI) Cu(II) Ni(II)	NA	Cr-10 Cu-3 Ni-1	80 min	NA	Cr-2.17 Cu-1.97 Ni-3.61	2	NA	100	The second stage of adsorption studies (i.e., without the reduction stage and two adsorption fixed-bed columns) proved to be more suitable for wastewater treatment than the first (i.e., with a first stage reduction of Cr and just one adsorption fixed-bed column)	(Calero and BI 2014)

Table 7 (continued)

Adsorbent	Heavy metal	Modifying agent	Initial conc. (mg/L)	Contact time (h)	Dose adsorbent	Adsorption capacity (mg/g)	Initial pH	Adsorption system	Removal efficiency (%)	Remarks	References
Microwaved olive stone activated carbon	Cd(II)	NA	1000	NA	NA	11.72	6.5–7	NA	95.32	Due to a large temperature difference between the interior of the char particle and its cold surface during microwave heating, the microwave-induced reaction can proceed quickly and effectively at a low bulk temperature; energy efficiency and a shorter processing time are the great features of microwave heating	(Alslaiibi et al. 2013)
Rice husk	Cd	NA	20–60	2	20, 30, 40, 50 and 60 (mg/L)	NA	6–7	NA	67.91	Rice husk was found to	(Hegazi 2013)
	Cu								98.17	be effective in the simultaneous removal of	
	Fe								99.25	Fe, Pb, and Ni in real	
	Pb								87.17	wastewater	
	Ni								96.95	The elimination of Cd and Cu was more effective with fly ash	(Hegazi 2013)
Fly ash	Cd	NA	20–60	2	20, 30, 40, 50, 60 (mg/L)	NA	6–7	NA	73.54		
	Pb								76.06		
	Fe								86.75		
	Ni								96.03		
	Cu								98.54		

**Table 7** (continued)

Adsorbent	Heavy metal	Modifying agent	Initial conc. (mg/L)	Contact time (h)	Dose adsorbent	Adsorption capacity (mg/g)	Initial pH	Adsorption system	Removal efficiency (%)	Remarks	References
Oxidized MWCNTs	Cr(VI)	NA	NA	165	NA	NA	2.05	NA	NA	On oxidized MWCNTs, Cr(VI) adsorption happens rapidly at first, then slowly as contact duration increases. Using MWCNTs as adsorbents to remove Cr(VI) from wastewaters takes a long time	(Hu et al. 2009)
Acidified MWCNTs	Pb(II)	NA	50	6	NA	NA	NA	NA	NA	Only 3.4% of the Pb(II) adsorption capacity is accounted for by PbO, Pb(OH) <sub>2</sub> , and PbCO <sub>3</sub> adsorbed on acidified MWCNTs	(Wang et al. 2007a)

Table 7 (continued)

Adsorbent	Heavy metal	Modifying agent	Initial conc. (mg/L)	Contact time (h)	Dose adsorbent	Adsorption capacity (mg/g)	Initial pH	Adsorption system	Removal efficiency (%)	Remarks	References
Groundnut husk	Cr(VI)	H <sub>2</sub> SO <sub>4</sub> , Ag impregnation	NA	5	NA	11.40	3	Batch	97	In terms of total Cr removal, silver impregnated groundnut husk carbon with an adsorption capacity of 11.399 mg/g exceeds groundnut husk carbon with a capacity of 7.0104 mg/g	(Dubey and Gopal 2007)

Table 7 (continued)

Adsorbent	Heavy metal	Modifying agent	Initial conc. (mg/L)	Contact time (h)	Dose adsorbent	Adsorption capacity (mg/g)	Initial pH	Adsorption system	Removal efficiency (%)	Remarks	References
Sawdust	Cr(VI)	HCl	0.1–100	NA	NA	1.74	3	Batch	84	Heavy metals could be removed using acid-modified sawdust.	(Argun et al. 2007)
	Ni(II)	HCl	0.1–100	NA	NA	1.74	8	Batch	82	Although its adsorption capacity per unit mass was lower than that of competitive substances such as ion-exchange resins and inactivated carbon, the material's high adsorption capacity per unit cost makes it a potential and cost-effective option	(Argun et al. 2007)
	Cu(II)	HCl	0.1 to 100	NA	NA	1.74	4	Batch	93		(Argun et al. 2007)
	Cu(II)	NA	5	24	5 (g/L)	1.79	7	Batch	85.2	A sawdust-based approach for removing and recovering heavy metal ions at the adsorption levels could be more cost-effective than current process technologies	(Yu et al. 2000)
	Cu(II)	NA	5	24	40 (g/L)	1.79	7	Batch	94.8		(Yu et al. 2000)
	Cu(II)	NA	50	24	5 (g/L)	1.79	7	Batch	58.6		(Yu et al. 2000)

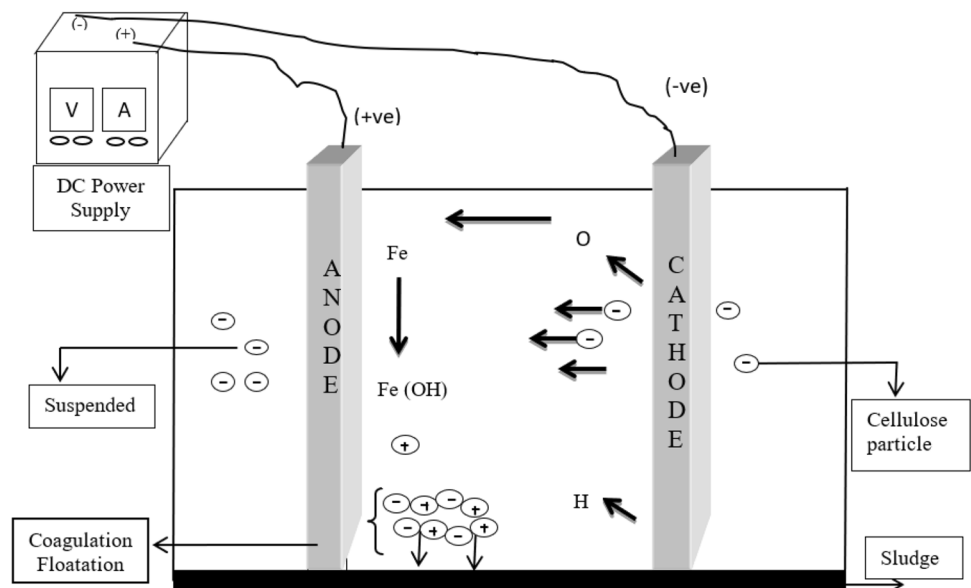
Electrocoagulation (EC), electrodeposition, electrofloatation (EF), electro dialysis (ED), and electrooxidation (EO) are the instantly applied techniques for reducing industrial effluents. Several patents have been found regarding this kind of electrochemical processes (Huang et al. 1989).

## Electrocoagulation

Over the previous two decades, an electro-coagulation method has been practiced to remove heavy metal ions such as As, Zn, Cr, Hg, Cd, Fe, Ni, Cu, and many others from industrial wastewater (Al-Qodah and Al-Shannag 2017). In the electro-coagulation process, coagulants are generated by electrolytic dissolution of Al or Fe ions from Al or Fe electrodes. The coagulants ions are produced at the anode, while hydrogen gas is released from the cathode to assist in the flocculation of the molecules (Fu and Wang 2011; Sharma et al. 2020a). The principle of the electro-coagulation method is shown in Fig. 7 (Zailani and Zin 2018). In contrast, to chemical coagulation, where several hours are required and adsorption on activated carbon, the electro-coagulation method attains faster removal of effluents from wastewater. However, Kamaraj et al. (2013) discussed the reduction process for Pb from aqueous solutions by electro-coagulation using magnesium as anode and galvanized iron as a cathode. With a current density of 0.8 A/dm<sup>2</sup> and a pH of 7.0, and an energy consumption of 0.72 kWh/m<sup>3</sup>, they were able to achieve a maximum removal efficiency of 99.3% for Pb. According to Kamaraj and Ganesan (2013), direct current was used in an EC method to extract Cu from water applying magnesium as both anode and cathode. Cu optimal removal performance

was obtained to be 97.8% and 97.2% at a current density of 0.025 A/dm<sup>2</sup> and pH of 7.0, with energy consumption of 0.634 and 0.996 kWh/m<sup>3</sup> for alternative current (AC) and direct current (DC), respectively. Furthermore, Al-Shannag et al. (2015) discussed the removal of Cu(II), Cr(III), Ni(II), and Zn(II) from metal plating wastewater by EC technique using Fe anodes. They found that using the pseudo-first-order model to evaluate the removal rates of these heavy metal ions is acceptable. The elimination efficiency rises as the EC residence time and DC density increase, according to their findings. The elimination effectiveness of heavy metal ions was 97% when using an EC treatment with a current density of 4 mA/cm<sup>2</sup>, a pH 9.56, and an EC time of 45 min. Akbal and Camcidotless (2011) investigated the removal of Cu, Cr, and Ni using Fe and Al electrodes in another investigation. The removal efficiency of heavy metal ions Cu, Cr, and Ni rise with increasing pH, current density, and conductivity. They used a Fe–Al electrode pair in an EC process to achieve 100% removal efficiency of Cu, Cr, and Ni at a current density of 10 mA/cm<sup>2</sup> and pH 3.0, with energy and electrode consumption of 10.07 kWh/m<sup>3</sup> and 1.08 kg/m<sup>3</sup>, respectively, and this removal efficiency increased due to hydrogen formation at the cathode and Al and Fe formation at the anode. However, Olmez (2009) used the RSM to investigate the impact of various operating parameters on the EC using stainless steel electrodes to remove Cr(VI) from industry effluent with a high concentration of 1470 mg/L. The study's findings confirmed that RSM was an appropriate method for optimizing operating settings such as 7.4 A applied electric current, 33.6 mM electrolyte sodium chloride concentration, and EC application period of 70 min for 100% Cr(VI) removal efficiency. In contrast

**Fig. 7** Principle electrocoagulation



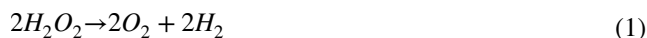
to the other treatment methods, electro-coagulation has many advantages such as it is fast, simple in operation, cost-effective, and environmental friendly (Ca et al. 2009).

## Electrodeposition

Electrodeposition, also known as electrowinning, is a redox reaction in which positively (+ve) charged metal ions (cations) are reduced and deposited at the cathode, and negatively (–ve) charged metal ions (anions) are oxidized at the anode. This approach is advantageous and reliable because no sludge is produced during the process, no additional reagents are required, a highly selective, cost-effective approach and no stable residues for metal recovery exist (Du et al. 2018). Organic contaminants in wastewater are destroyed at the anode while heavy metals are reduced and electroplated at the cathode during the electrodeposition process (Chang et al. 2009). An integrated methodology combining ultrasound and an electrodeposition method was employed to treat EDTA-copper wastewater. Cu removal efficiencies of 95.6% w/w follow the order of  $\text{pH } 3 > \text{pH } 5 > \text{pH } 7$ , with different voltage gradients following the order of  $2.0 \text{ V/cm} > 1.5 \text{ V/cm} > 1.0 \text{ V/cm} > 0.5 \text{ V/cm} > 0.5 \text{ V/cm}$ , showing that it is the most efficient wastewater treatment technology (Chang et al. 2009).

## Electrofloatation

EF is a solid/liquid separation technique that incorporates the production of hydrogen and oxygen gases from water electrolysis in the form of small bubbles due to the pollutants floating to the water body's surface. EF has a variety of applications that have a lot of potential for removing heavy metals from industrial effluent. Wastewater effluents float to the surface of the liquid phase, where they can be easily separated using this EF process. In the total reaction, water electrolysis produces oxygen and hydrogen in the solution (Chen 2004):



The heavy metal particles adhere or adsorb to the oxygen and hydrogen molecules, causing the emulsified particles to be dismissed and flocs to form (Oliveira et al. 2014). The separation for the settling of the settled flocs and flotation of generated foam is carried out in the second step. In the third step, the collected pollutants are removed by filtration methods. Kolesnikov et al. (2015) investigated the effect of several surfactants on the physicochemical parameters of the dispersion phase for the removal of Cu, Ni, and Zn hydroxides at concentrations of 2, 10, 50, and 100 mg/L at pH

9.5–10.5. Anti-wear oxide electrodes were used to achieve a removal efficiency of more than 95% with a current density of roughly 0.2 A/L and a processing time of about 30 min.

On the other hand, Sun et al. (2009) discovered that employing Fe electrodes in combination with filter paper, micro, and UF bench-scale experiments could give excellent residual Ni, Fe, and turbidity results both with and without the addition of external oxygen. The residual Ni and Fe might meet the metal finishing industry's discharge regulations with the hybridization of EF without aeration followed by microfiltration and aeration-enhanced EF followed by settling and paper filtration, according to their results. They came to the conclusion that combining an aeration-enhanced EF method with microfiltration could provide higher Ni and Fe removal results. Because this technology does not produce secondary pollution, it is particularly effective in the local water purification system.

## Electrodialysis

Desalination research in the 1950s led to the development of ED (Azimi et al. 2017). ED is an ion-exchange membrane separation technique in which ionized species in a solution are transported through it while an electric potential is applied (Bruggen and Vandecasteele 2002). When ionic species in the solution pass through the cell compartments, they cross anion-exchange and cation-exchange membranes. At the same time, the anions and cations attract towards the anode and cathode, respectively (Barakat 2011). Tzanetakakis et al. (2003) found some interesting results when they tested the effectiveness of ion exchange membranes for the ED of Ni(II) and Co(II) ions from a synthetic solution. Two cation exchange membranes, sulfonated polyvinylidene fluoride membrane (SPVDF) and perfluorosulfonic Nafion 117 were utilized and compared under similar working conditions. The removal efficiencies of Co(II) and Ni(II) using the perfluorosulfonic Nafion 117 membrane were 90% and 69%, respectively, with initial metal concentrations of 0.84 and 11.72 mg/L. Nataraj et al. (2007), on the other hand, constructed and operated an ED pilot plant that included a set of ion-exchange membranes and a new working system to test the rejection of Cr(VI) ions. Variations in applied potential, pH, initial Cr concentration, and flow rates were used to test the ED unit's ability. With lower initial concentrations of less than 10 ppm, satisfactory results were obtained in meeting the maximum contaminant limit (MCL) of 0.1 mg/L for Cr.

ED has a number of benefits, including the ability to produce a highly concentrated stream for recovery and the ability to remove undesired effluents from water. Furthermore, it can be utilized to treat wastewater containing important metals like Cr and Cu. Because ED is a membrane process,



it requires a clean feed, careful operation, and regular maintenance in order to avoid stack damage (Barakat 2011).

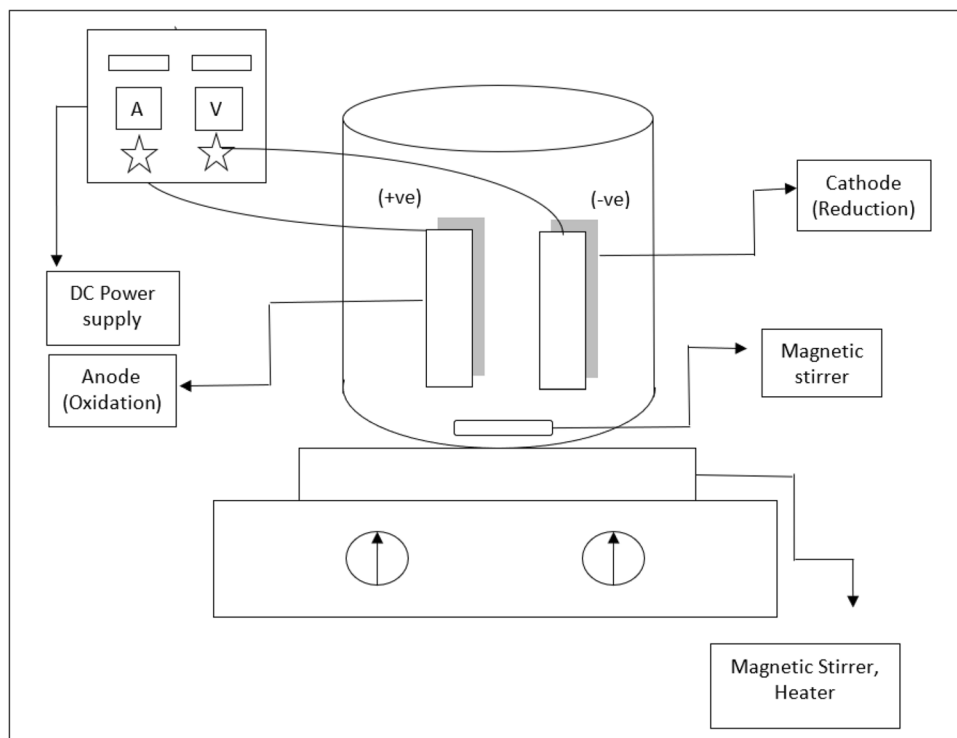
## Electrooxidation

When electrochemical decomposition of CN was noticed in the late nineteenth century, an extensive study on EO for wastewater treatment was conducted (Kuhn 1971). In general, an electrochemical process comprises of redox processes occurring at both the anode (e.g., pollutant oxidation) and cathode (e.g., heavy metal reduction). The basic idea behind this technique is to take advantage of eliminating contaminants, which has long been used as a heavy metal remediation method (Nancharaiah et al. 2015). The electrochemical advanced oxidation processes (E-AOP) have raised the focus of research and application for electrochemical oxidation methods, which aim to mineralize organic molecules in process water and wastewater (Muddemann et al. 2019). Most of them are patents, including the electrolytic advance oxidation processes to treat wastewater, as reported by (Haddad 2013). Electrochemically generated oxidants can be found directly on the anode oxidants surface or indirectly through subsequent reactions with inorganic components (Botte 2017). Figure 8 illustrates the basic principle of EO. The anode (M), which involves direct charge transfer processes between the anode surface and organic pollutants in water, is the source of direct anodic oxidation or electrolysis. Only the arbitration of electrons, which can oxidize some

organic contaminants at particular potentials lower than the oxygen evolution reaction (OER) potential, constitutes the mechanism (Garcia-Segura et al. 2018). However, the growth of polymeric coatings on their surface causes electrode fouling and results in poor chemical decontamination in this procedure. The indirect oxidation approach, which has an advantage over the direct oxidation method, depends on the oxygen evolution region that can be employed to overcome the issues of direct oxidation. It produces no waste and does not demand the use of oxidation catalysts in the solution. Physically adsorbed “active oxygen” (adsorbed hydroxyl radicals,  $\bullet\text{OH}$ ) or chemisorbed “active oxygen” (oxygen in the oxide lattice,  $\text{MO}_{x+1}$ ) can potentially result in direct electrooxidation of pollutants on anodes. According to a survey of research literature, the EO process is environmentally friendly and highly efficient for organic/inorganics pollutants elimination. This process was used to extract CN wastes that were exceedingly concentrated (50,000 mg/l  $\text{CN}^-$ ). During EO, metals can be collected at the cathode while CN ions are destroyed at the anode (Cheng et al. 2002).

On the other hand, Valiūnienė et al. (2015) used a Ti electrode covered with a 600 nm average thickness of Pt as a cost-effective anode to examine the EO process for CN ion removal from wastewater. The effective EO of a highly concentrated CN solution (2600 mg/L, or 0.1 M KCN) approaches a constant value of 3.45 V when a current density of 25 mA/cm<sup>2</sup> is applied. The CN ions are practically eliminated (from 0.1 to 0.00016 M) when 60%

**Fig. 8** Electrooxidation process



current efficiency is attained, and 69 kC/L of charge is conveyed. Szpyrkowicz et al. (1998) employed stainless steel electrodes for the simultaneous EO of CN and Cu recovery. Their results displayed that at pH 13, the direct electrooxidation process was suitable and economically convenient. They also investigated reducing Cu concentration from 470 mg<sup>-1</sup> by 79% in 1.5 h, at an energy consumption of 17 kWh/q, and recovering 335.3 mg of Cu as a pure metal electrodeposited on the cathode. In a recent study, Kazeminezhad and Mosivand (2017) examined the use of Fe sacrificial sheets in an electrolytic cell to eliminate Ni and Cu from effluent. Heavy metal concentrations were resolved using an AAS instrument. The results of the AAS demonstrated that increasing the applied voltage, electrochemical reaction duration or pH efficiently reduces the content of heavy metal contaminants in the water. It can greatly reduce Ni or Cu concentration in water when applied at 28 V for 60 min at pH 4.5. Table 8 shows the results of some study on the removal of heavy metals from industrial effluent using electrochemical methods.

## Advanced oxidation processes

AOP has grown in popularity in recent years and is now widely employed to treat industrial wastewater (Korpe et al. 2019). It is a powerful treatment technique that uses hydroxyl radicals (OH•) to eliminate refractory organic pollutants effectively. The creation of hydroxyl radicals (HO•) from hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), ozone, photocatalysis, or oxidants in combination with the use of ultraviolet (UV) radiation is the basic principle of AOP. Two or more radical generators are sometimes used in combination. The HO•, on the other hand, is primarily responsible for the organic compound breakdown. It targets practically all organic complexes once it is generated. As a result of the HO• attack, the organic component is completely broken down, and AOPs reduce the pollutant concentration from a few hundred ppm to less than 5 ppb (Mohajerani et al. 2009). AOPs should, in theory, totally mineralize organic molecules to (CO<sub>2</sub>) and (H<sub>2</sub>O). The Photocatalysis AOP and electro-Fenton technique are the most commonly utilized in water treatment.

## Photochemical advanced oxidation process

Photocatalysis is a type of photochemical AOP that has a lot of potential due to its ease of application, inexpensive, high degradation rate, low toxicity, and high stability. Semiconductor photocatalysis, first invented in 1972, is a new wastewater treatment process. Semiconductor photocatalysis, which uses UV-irradiated titanium dioxide (TiO<sub>2</sub>) to detoxify toxic materials in the aqueous phase, is already a

well-established topic of research (Xu et al. 2006; Meichtry et al. 2007). It has received a lot of interest as a possible solution for wastewater treatment and environmental protection. The electronic structure and photoelectric characteristics of TiO<sub>2</sub> are responsible for its catalytic activity. The band theory can be used to describe the photocatalytic reaction concept (Robert et al. 2004). TiO<sub>2</sub> has a valence band and a conduction band, with a bandgap energy of 3.2 eV. When the surface of TiO<sub>2</sub> is irradiated with light equal to or greater than the bandgap energy of TiO<sub>2</sub>, the surface is stimulated, resulting in the production of a hole-electronic pair with oxidation and reduction abilities. Expression is the same as Eq. (2).



The produced h<sup>+</sup> can oxidize OH<sup>-</sup> and H<sub>2</sub>O on the TiO<sub>2</sub> surface to OH, and OH can almost totally oxidize all pollutants deposited on the TiO<sub>2</sub> surface. Any metal ions with a reduction potential greater than the edge of the TiO<sub>2</sub> conduction band can theoretically be reduced by e<sup>-</sup>. The photocatalytic mechanism of TiO<sub>2</sub> semiconductor is shown in Fig. 9 (Jiang et al. 2012). The series of reactions involved in the photocatalytic process are as follows:



Several semiconductor photocatalysts have been examined and reported, like titanium dioxide (Tryba et al. 2019), zinc oxide (Shen et al. 2008), tungsten trioxide (Yu et al. 2008), and cadmium sulfide (Di et al. 2009). The application research of TiO<sub>2</sub> photocatalytic degradation of organic contaminants has been an interesting subject since the late 1960s. Various findings show that TiO<sub>2</sub> is highly promising than the other semiconductor photocatalysts for applications in air purification, water decontamination, adsorption of contaminants (Tanzifi et al. 2018), and treatment of wastewater (Shahrezaei et al. 2012) due to its properties like low cost, non-corrosivity, high chemical resistance, and antioxidant ability. PC has proven its applications in various environmental fields like removal of aqueous pollutants and metal removal or/and recovery. Organics and inorganics (heavy metal ions, CN-containing waste, NO<sub>2</sub>-containing waste, and so on) can be destroyed simultaneously using this method (Schrack et al. 2002). Photocatalytic reduction and

**Table 8** Removal efficiency of heavy metal treatment by electrochemical methods

Method	Heavy metal	Electrolyte	Initial conc. (mg/L)	Type of electrode	Current density	Contact time	Initial pH	Removal efficiency (%)	Remarks	References
EC	Cr, Pb	NA	Cr-55.3 Pb-3.5	Iron (Fe)	73.5 A/m <sup>2</sup>	90 min	3.5	Cr-91.7 Pb-91.3	Anode consumption increased with a decrease in pH in the EC treatment. As the pH level increased, so did the amount of energy consumed	(Sharma et al. 2020b)
EC	Cu, Ni, Zn, Cr	NaCl	20	Aluminum (Al) and Fe	2.0 and 4.0 mA/cm <sup>2</sup>	1 h	9	>90	Due to the reduction of Cr <sup>6+</sup> ions by Fe <sup>2+</sup> ions produced by the electrode; the Fe electrode had a higher removal efficiency for Cr than the Al electrode	(Kim et al. 2020)
Electrodeposition	Ni	Na <sub>2</sub> WO <sub>4</sub>	0.1 M	Copper	100 A/m <sup>2</sup>	24 h	NA	100	—	(Porto et al. 2020)
EC	Cr, Cu, Zn	H <sub>2</sub> SO <sub>4</sub> NaOH NaCl	50	(Al)		60 min	4	Cr-87.6 Cu-100 Zn-99.2	The % of heavy metals removed increased as the electrocoagulation time, NaCl concentration, and applied electric current increased	(Ayub et al. 2020)
EC	Zn, Cr, Ni, Cu	NaOH and H <sub>2</sub> SO <sub>4</sub>	Zn-35 ± 3, Cr-250 ± 1 Ni-75 ± 5, Cu-75 ± 5	Al and Fe	175 A/m <sup>2</sup>	40 min	1.8–4.08	Zn-98.3 Cr-95 Ni-56 Cu-26.6	Fe was excellent in removing chromium and copper as compared to the Al electrodes	(Ilhan et al. 2019)

Table 8 (continued)

Method	Heavy metal	Electrolyte	Initial conc. (mg/L)	Type of electrode	Current density	Contact time	Initial pH	Removal efficiency (%)	Remarks	References
Electrodeposition	Mn(II)	Na <sub>2</sub> SO <sub>4</sub>	100	SS	4 mA/cm <sup>2</sup>	120 min	7.5	<99	Time > current density (CD) > mesh number > initial Mn conc. Were the most important operating parameters, with contributions of 47.42, 37.13, 5.73, and 0.05%, respectively	(Salman 2019)
EC	Cr, Ni, Zn	NA	Cr-358 ± 2.1 Ni-8.1 ± 0.3 Zn-149.3 ± 2.1	Iron	30 mA/cm <sup>2</sup>	30 min	5	Cr-98.9 Ni-96.3 Zn-99.8	The EC process may provide outstanding heavy metal removal, and RSM is potent for optimizing operational parameters	(Oden and Sari-Erkan 2018)
EO	Cu, Ni	NA	NA	Iron	NA	60 min	4.5	NA	--	(Kazeminezhad and Mosivand 2017)
EO-electrodeposition	Ni	NA	NA	RuO <sub>2</sub> /Ti	32	90 min	9	99	The EO technique is effective at removing Ni-ammonia compounds and recovering Ni from wastewater by electrodeposition	(Guan et al. 2017)

Table 8 (continued)

Method	Heavy metal	Electrolyte	Initial conc. (mg/L)	Type of electrode	Current density	Contact time	Initial pH	Removal efficiency (%)	Remarks	References
EC	Pb	NA	500	Al-Al	2.67 mA/cm <sup>2</sup>	30	5	99	EC could be applied as a cost-effective process to remove Pb from wastewater with high removal	(Bouguerra et al. 2015)
Electrodeposition	Ni	H <sub>2</sub> SO <sub>4</sub>	2402.19	Graphite	NA	4 h	NA	27	According to the observations, the partitioned reactors using water hyacinth leaf worked better than the single-chamber reactor	(Djaenudin et al. 2015)
EC	As(III)	NA	50	Al-Al	1.54 mA/cm <sup>2</sup>	NA	4	85	--	(Zeliha et al. 2015)
EC	Cu, Ni, Zn	NA	250	Fe/vertical	15 mA/cm <sup>2</sup>	50	5.5–5.7	96	In comparison to chemical	(Al Aji et al. 2012)
EC	Mn	NA	250	Fe/vertical	15 mA/cm <sup>2</sup>	50	5.5–5.7	72.6	coagulation, which takes several hours, and adsorption on activated carbon, EC utilizing	(Al Aji et al. 2012)
EC	Cr, Cu	NA	50–250	Al	25 mA/cm <sup>2</sup>	15	4	99.9	monopolar iron electrodes provides a practical way to effectively remove heavy metals from a model effluent and achieve rapid removal of pollutants	(Al Aji et al. 2012)
EC	Zn	NA	50–250	Al/parallel	25 mA/cm <sup>2</sup>	15	4	83		(Al Aji et al. 2012)

Table 8 (continued)

Method	Heavy metal	Electrolyte	Initial conc. (mg/L)	Type of electrode	Current density	Contact time	Initial pH	Removal efficiency (%)	Remarks	References
EC	Cd	NA	1.5	Al-SS	NA	NA	66		The sacrificial anode corroded in the electrochemical process, releasing Al <sup>3+</sup> , which served as a coagulant for the precipitation of chelant and metals	(Pociecha and Lestan 2010)
EC	Pb	NA	170	Al-SS	16–128 mA/cm <sup>2</sup>	7.52	95			
EC	Zn	NA	50	Al-SS	16–128 mA/cm <sup>2</sup>	7.52	68			
EC	Zn	NA	NA	Al/Fe	60 mA/cm <sup>2</sup>	25	Fe-3 Al-5	Fe-97.8 Al-96.7	In comparison to Al electrodes with energy consumptions of 0.18–11.29 kWh/m <sup>3</sup> , Fe electrodes with energy consumptions of 0.24–8.47 kWh/m <sup>3</sup> were more efficient in the same current density range	(Kobyta et al. 2010)

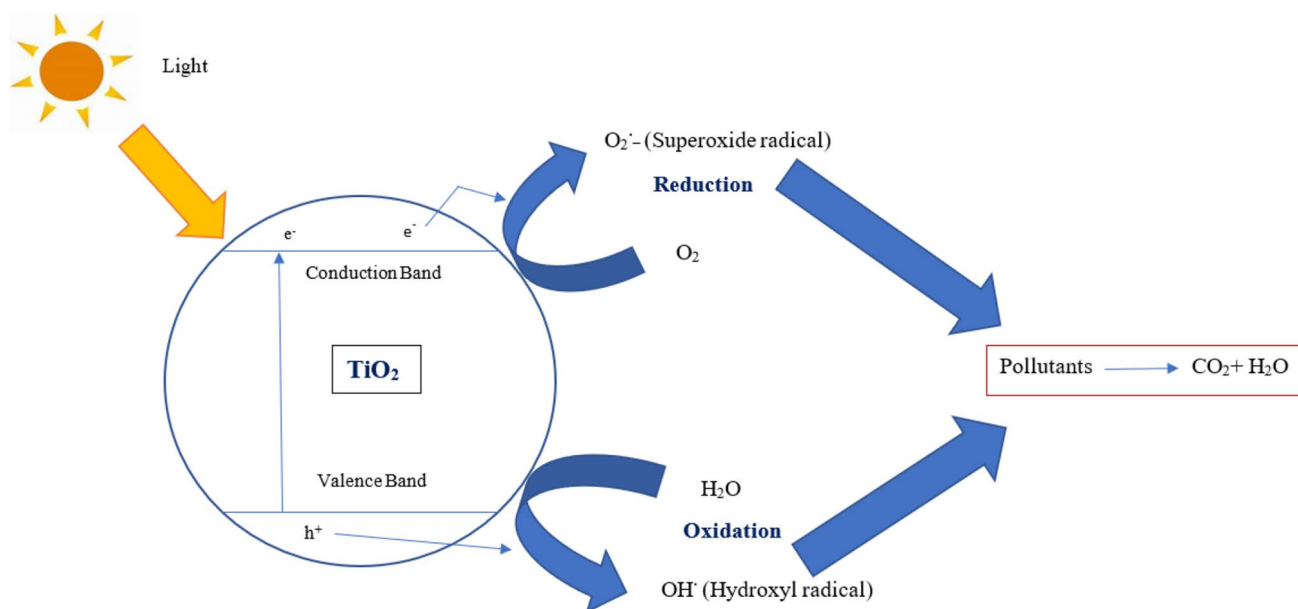
Table 8 (continued)

Method	Heavy metal	Electrolyte	Initial conc. (mg/L)	Type of electrode	Current density	Contact time	Initial pH	Removal efficiency (%)	Remarks	References
Electrodeposition	Cu(II)	NA	110	NA	NA	220	3	79.18	According to the observations, ultrasonication combined with electrode placement can successfully remove Cu (95.6%) and break down EDTA (84% COD elimination) from wastewater containing an EDTA–Cu combination	(Chang et al. 2009) (Chang et al. 2009)
Electrodeposition	Cu(II)	NA	110	NA	NA	220	7	56.09		
EC	Cr(VI)	NA	20–100	Fe-Al	6.7–26.7 mA/cm <sup>2</sup>	20–100	8	97	When compared to standard EC, the use of granular activated carbon (GAC) as an adsorbent resulted in a considerable improvement in the Cr removal rate at lower current density and operating time	(Narayanan and Ganesan 2009)

Table 8 (continued)

Method	Heavy metal	Electrolyte	Initial conc. (mg/L)	Type of electrode	Current density	Contact time	Initial pH	Removal efficiency (%)	Remarks	References
EC	Cr(III)	NA	NA	Bipolar electrode configuration	NA	50	NA	99.9	When compared to monopolar electrode designs, EC with bipolar electrode configuration significantly improves the removal of Cr(III) at higher pH due to the combined action of chemical precipitation, co-precipitation, cathodic reduction, and adsorption	(Golder et al. 2007)
EF	Cu	NA	50	NA	NA	60	5	99	Heavy metal removal achieved	(Khelifa et al. 2005)
EF	Cu	NA	500	NA	NA	60	5	71	98–99% after optimizing the operation, and final and global concentrations were kept below the WHO limit of 1 ppm for Ni and Cu	(Khelifa et al. 2005)
EF	Cu	Sodium sulfate	500	NA	NA	60	5	99		(Khelifa et al. 2005)
EF	Cu	NA	100	NA	NA	15 min	5	57		(Khelifa et al. 2005)
EF	Ni	NA	100	NA	NA	5 h	6	37		(Khelifa et al. 2005)
EF	Ni	Sodium sulfate	100	NA	NA	5 h	6	81		(Khelifa et al. 2005)



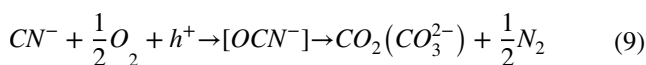


**Fig. 9** Mechanism of photocatalysis

photocatalytic oxidation are the most common mechanisms for the elimination of inorganic contaminants. Cr(VI), Hg(II) and Pb(II) are currently the focus of additional study on photocatalytic remediation of metal ions contaminants in effluent (Kabara et al. 2008; Luo et al. 2017) Eq. (8) depicts the photocatalytic pathway for heavy metals ( $Mn^{+}$  denotes metal oxide, and  $M$  denotes the photocatalysis product).



Cyanide (mainly free cyanogen root) is highly hazardous and is primarily produced by the electroplating industry. In specific fields, cyanide emissions have recently grown. Photocatalysis with  $TiO_2$  may effectively convert poisonous  $CN^{-}$  to  $CO_2$  or  $CO_3^{2-}$  and harmless  $N_2$ . The reaction is written as follows: (9).



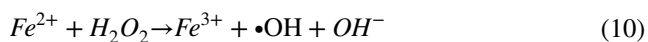
The sol-gel method was used to make a new photocatalyst,  $TiO_2$  doped with neodymium (Nd), which was used to reduce Cr(VI) photo-catalytically under UV irradiation (Rengaraj et al. 2007). According to the findings, adding Nd (III) to  $TiO_2$  catalysts increases the photocatalytic reaction of Cr(VI) reduction substantially. On the  $TiO_2$  surface, Nd ions serve as electron accumulation sites. Charge carriers can be routed more efficiently towards favorable reduction and oxidation events rather than recombination reactions due to the better separation of electrons and holes on the modified  $TiO_2$  surface. The inclusion of sacrificial electron donors, such as formic acid aids photocatalytic reduction. Cr(VI) adsorbed

on the surface of  $TiO_2$  particles was found to be nearly completely photo-reduced. A novel anodization-based immobilization technique was applied and tested to overcome the limitations of powder  $TiO_2$  (Yoon et al. 2009). An immobilized  $TiO_2$  electrode was employed to convert dangerous Cr(VI) to non-toxic Cr(III) in an aqueous solution under UV irradiation. The anodized samples were annealed in an oxygen stream at temperatures ranging from 450 to 850 °C after being anodized with 0.5% hydrofluoric acid. Photocatalytic Cr(VI) reduction was found to be helpful under acidic conditions, with 98% of the Cr(VI) being reduced after 2 h at pH 3 (Yoon et al. 2009).

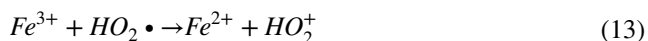
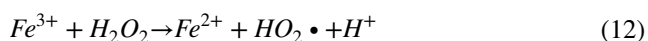
### Electro-Fenton process

The electro-Fenton method is one of the (E-AOP), and it has been found to be energy efficient for wastewater treatment as an improved Fenton process. The interaction of polycarboxylic acid with hydrogen peroxide ( $H_2O_2$ ) was found in the 1890s by Fenton H.J.H., who observed a substantial promotion in the existence of ferrous ions ( $Fe^{2+}$ ). An oxidant, usually  $H_2O_2$ , and a catalyst, generally Fe in the form of  $Fe^{2+}$  are used in the Fenton process, also known as dark Fenton. The oxidation of  $Fe^{2+}$  results in the formation of  $\bullet OH$ . Simultaneously, in the electro-Fenton approach, the strong  $\bullet OH$  radicals created by the catalytic breakdown of electrogenerated  $H_2O_2$  in the treated solution facilitate the destruction of organic pollutants (Asgari et al. 2016). Adding a redox couple to the system causes  $H_2O_2$  to decompose into highly reactive  $\bullet OH$  radicals (Aramyan 2017). For the

electro-Fenton procedure, the  $Fe^{2+}/Fe^{3+}$  couple produces the best results (Pimentel et al. 2008).



The process can be propagated by regenerating  $Fe^{2+}$  by chemical or electrochemical processes (Eqs. (11)–(14)) (Umar et al. 2010).



Anodic oxidation, cathodic reduction, neutralization, and electrodeposition may be included in the reaction mechanism, with the metal complex elimination procedure employing electro-Fenton displayed in Fig. 10.

As a result, electro-Fenton offers several distinct advantages: high removal efficiency, simplified reactor structure, increased wastewater organic degradability, continuous generation of  $H_2O_2$  from  $O_2$  reduction or  $Fe^{2+}$  from the Fe anode, lowering treatment costs, the minimization of secondary pollution, the requirement to adjust current (A) and voltage (V) throughout the electrolysis process (Xu et al. 2021). The fact that this procedure happens in acidic media and that Fe removal is necessary are the key applicative limitations. The electro-Fenton process highly depends on

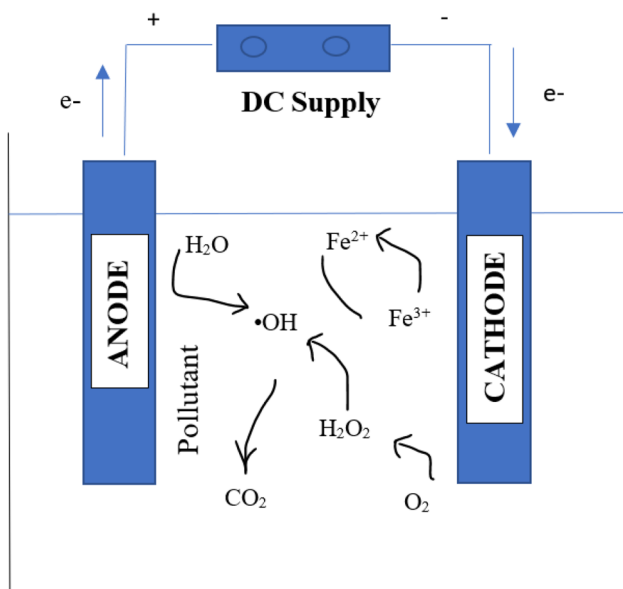


Fig. 10 Mechanism of the electro-Fenton method

electrode materials, and considerable work has gone into selecting appropriate conductive materials to optimize metal complex removal (Burgos-Castillo et al. 2018; An et al. 2019). Carbon felt cathodes were changed by doping with pyridinic N (Zhou et al. 2020). This alteration produced a large number of active sites by producing near-ring defects in the heterogeneous electro-Fenton process for purification of Ni(II)-EDTA by replacing C=C groups with nitrogen, which greatly reduced  $H_2O_2$  consumption and raised the utilization ratio.

However, the electro-Fenton process has some advantages, such as electro-Fenton's reagent is inexpensive, the procedure is simple to set up and maintain, the activation of  $H_2O_2$  does not require any energy, short reaction time among all AOP. Some drawbacks include electrode material resistance, high energy consumption needs, low current efficiency, and  $Fe^{2+}$  is used at a faster rate than it is regenerated. As a result, further investigation is necessary on 3D electrode materials because they offer significant benefits in terms of improving current efficiency and lowering energy consumption (Hou et al. 2015; Peng et al. 2015).

## Comparison of electroplating wastewater treatment technologies

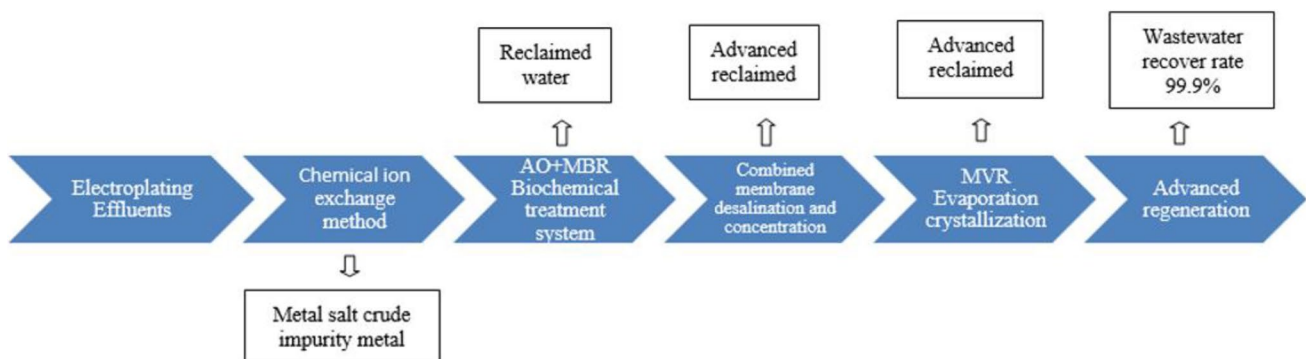
Various techniques applied for waste streams generated from the electroplating industry have been considered and are equally important for detecting industrial effluents. Overall, each treatment process has its own set of benefits and drawbacks. The pros and cons of the different conventional and advanced treatments studied in this research are summarized in Table 9.

## Status of “zero emission” of electroplating wastewater

Designing alternative industrial wastewater treatment solutions involving hazardous and non-biodegradable organic substances that cannot be fully oxidized as a traditional approach has been a major concern. Most of these physicochemical approaches (i.e., chemical precipitation, coagulation, flocculation, etc.) have proved unsatisfactory due to the high complexity of the industrial effluents. Due to the inadequacy of physicochemical techniques, economic, legal, social, and environmental demands have increased to adopt the excellent technology at reduced prices and seek “zero discharge.” Today, “zero emissions” has evolved into a problem that we are deeply concerned about. Finally, various companies have performed substantial research into what technologies may be used to achieve “zero-emission” of electroplating effluent (Figs. 11 and 12). To achieve zero

**Table 9** Advantages and disadvantages for electroplating wastewater treatment methods

Techniques	Advantages	Disadvantages	References
Coagulation–flocculation	<ul style="list-style-type: none"> <li>• Ease sludge settling</li> <li>• Cost-effective</li> <li>• Dewatering qualities</li> </ul>	<ul style="list-style-type: none"> <li>• Generation of sludge</li> <li>• Sludge disposal involves high operational costs</li> </ul>	(Ahmed and Ahmaruzzaman 2016)
Ion-exchange	<ul style="list-style-type: none"> <li>• Removal efficiency is high</li> <li>• Fast kinetics</li> <li>• No sludge generation</li> <li>• High treatment capacity</li> <li>• Less time consuming</li> </ul>	<ul style="list-style-type: none"> <li>• High resin cost</li> <li>• Slow operation rate</li> <li>• Regenerations of resins</li> <li>• High capital and operational cost</li> </ul>	(Islamoglu et al. 2006)
Chemical precipitation	<ul style="list-style-type: none"> <li>• Ease of operation</li> <li>• Low capital cost</li> </ul>	<ul style="list-style-type: none"> <li>• Produces large quantity of sludge</li> <li>• Sludge disposal problems</li> <li>• Ineffective with the low concentration of metal ions</li> </ul>	(Azmi et al. 2018)
Membrane filtration	<ul style="list-style-type: none"> <li>• High removal efficiency</li> <li>• Need less space</li> <li>• Low operating pressure</li> </ul>	<ul style="list-style-type: none"> <li>• Membrane fouling</li> <li>• Complexity in process</li> <li>• High operating cost</li> </ul>	(Ahmed and Ahmaruzzaman 2016)
Adsorption	<ul style="list-style-type: none"> <li>• Attractive</li> <li>• Simple</li> <li>• Inexpensive</li> </ul>	<ul style="list-style-type: none"> <li>• Low selectivity</li> <li>• Limited to certain concentrations of metal ions</li> <li>• Adsorbent regeneration is difficult</li> </ul>	(Golder et al. 2008)
Electrochemical methods: EC (electrocoagulation)	<ul style="list-style-type: none"> <li>• High energy efficiency</li> <li>• High selectivity</li> <li>• High capacity</li> <li>• Cost-effectiveness</li> </ul>	<ul style="list-style-type: none"> <li>• High operating cost</li> <li>• Periodically change of sacrificial anodes</li> <li>• Sludge production problem</li> </ul>	(Meas et al. 2010; Rodrigo et al. 2010)
ED (electrodialysis)	<ul style="list-style-type: none"> <li>• High capacity</li> <li>• High separation selectivity</li> </ul>	<ul style="list-style-type: none"> <li>• Clean feed is necessary</li> <li>• Proper maintenance to avoid stack damage</li> <li>• Expensive because it needs costly membranes</li> </ul>	(Malaviya 2011)
EO (electrooxidation)	<ul style="list-style-type: none"> <li>• Total removal of persistent organic pollutants</li> <li>• Eco-friendly in nature</li> <li>• It is simple to integrate with other conventional techniques</li> <li>• Produce less sludge, high separation</li> </ul>	<ul style="list-style-type: none"> <li>• High operating cost</li> <li>• Higher current density</li> </ul>	(Garcia-Segura et al. 2018)
AOP	<ul style="list-style-type: none"> <li>• Can treat nearly all organic compounds and heavy metals</li> <li>• No sludge generation</li> <li>• Does not concentrate waste for further step</li> </ul>	<ul style="list-style-type: none"> <li>• Relatively high capital and operating/maintenance costs</li> </ul>	(Guan et al. 2020)

**Fig. 11** Zero discharge of electroplating wastewater

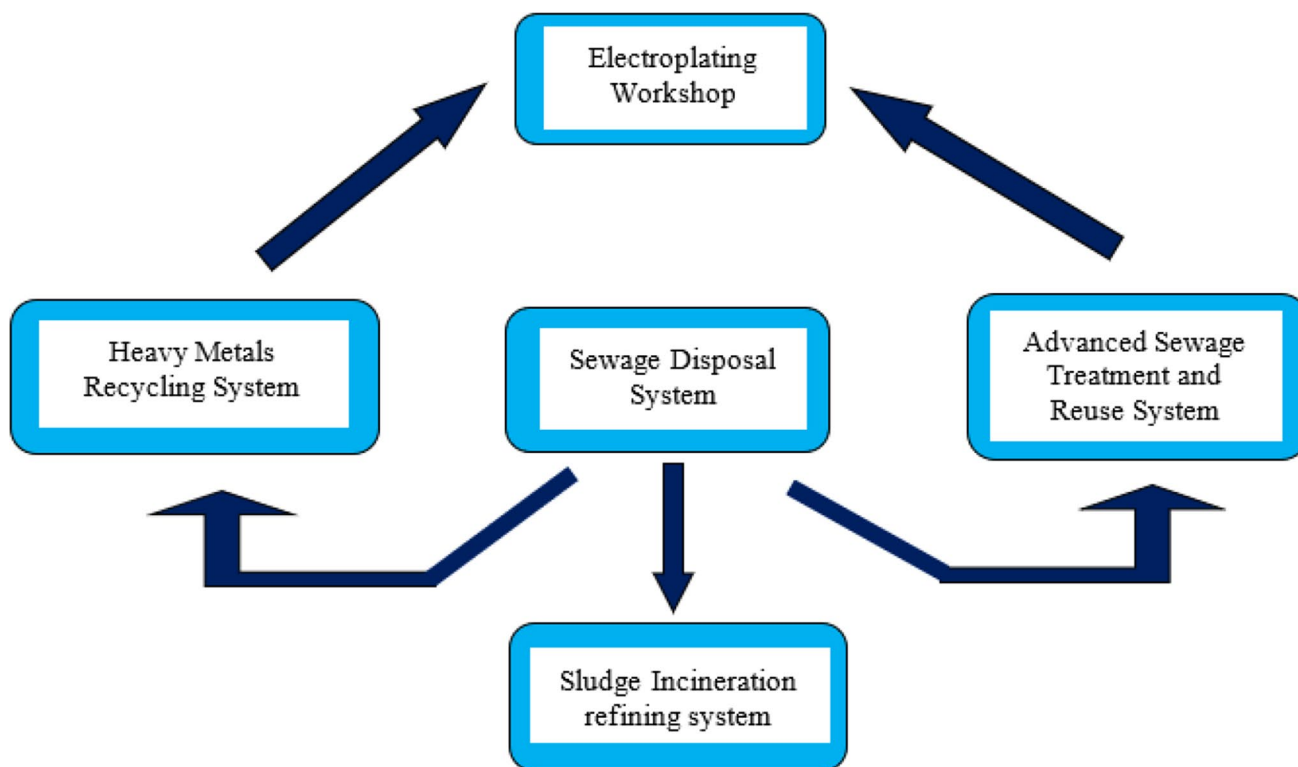


Fig. 12 Recycling of heavy metals

discharge, wastewater reuse, metal salt recycling, and other challenges must be addressed first (Lu and Wu 2020).

### Future prospective

The development of efficient and ecologically friendly wastewater treatment systems is being aided by rising environmental concern and social awareness of the health issues and ecosystem impacts of industrial contaminants. Most techniques with proper operation can lead to answerable for the electroplating wastewater treatment. Recovery of heavy metal ions and effective treatment of electroplating industry effluents is not feasible economically. Before the selection of treatment method, a complete analysis of any particular plant and wastewater generated.

More research study is still required for each technique to develop it and make it more appropriate. Inventive methods are needed to advance cheap, readily available, superior, and long-lasting membranes for membrane filtration. As for electro-dialysis, the improvement of new designs is necessary to progress the separation efficiency. Because most of the literature evaluated in this work is limited to an initial estimation of removal efficiency, it is critical to pursue further investigations at the pilot-plant size. As a result, the authors believe that more research

is needed to establish feasible technology at a range of scales for applications at various locations and scales around the world and better understand the industrial effluent rejection phenomenon. More research into these methods should focus on testing them with real wastewater and operating them in a continuous mode to allow for progressive scaling up. Batch treatment systems have fewer industrial uses than continuous treatment systems. The majority of literature studies are done in batch systems; hence there is a need to develop continuous systems.

The electrode material chosen is important since it impacts the selectivity and efficiency of the electrochemical process. In other words, anode materials are the essential part of the electrode, as they regulate the with which pollutants are oxidized. More research on electrocatalytic anodic materials is needed to concentrate on lowering the initial costs of electrode purchase.

The future of wastewater treatment implies a combination of numerous process and advanced treatment methods (i.e., AOP). As a result, hybrid procedures or a combination of modern electrochemical techniques and other chemical/biological methods are urgently needed, where a reasonable compromise between acceptable economic cost, high removal efficiency, and environmental responsibility can be reached.

## Conclusions

Electroplating wastewater treatment for the elimination of industrial effluents such as heavy metals has seen significant performance in recent years and witnessed vast advancement in applications and technologies. Generally, a vast amount of research has been carried out by a more significant number of researchers to remove metals ions from industrial wastewater by applying many various technologies. Nowadays, one major challenge is finding the most cost-effective, efficient, and appropriate method for removing hazardous contaminants from water bodies. Most conventional techniques (e.g., chemical precipitation, coagulation, and flocculation) have proven ineffective due to the high complication of industrial wastewater composition. Due to the inadequacy of traditional approaches, economic, social, legal, and environmental demands have increased to apply the best technology at reduced prices and seek “zero discharge.” Each technique has its own benefits/drawbacks, with different removal efficiencies as well as characteristics influencing the removal process. The variable parameters altered removal efficiencies of Cd, Mn, Ni, Fe, and As from 47 to 99%, while complete removal of some metals (i.e., Cu, Pd, Cr, and Zn) which was examined from different technique results and their experimental condition. The removal efficiency of heavy metals (47–100%) and reducing their dosage to standard limits under optimum conditions were achieved using RO, UF, electroflotation, and electrocoagulation.

The following conclusions could be drawn from the various techniques which are discussed in the review:

1. Chemical precipitation is a simple and cost-effective way to treat industrial effluent. It has drawbacks, such as the operational cost being high due to the sludge disposal. This approach is extensively used when heavy metal concentrations are high, but it is inadequate when metal ions concentrations are low. While the coagulation/ flocculation process has a high removal efficiency, it also produces secondary contaminants, which transfer the harmful compounds into the environment. During this treatment, the formation of sludge appears, which must be handled finally.
2. An ion-exchange process is another method for treating industrial wastewater. This technology has a minimal maintenance cost and produces an excellent flow rate of treated water. However, ion exchange has some benefits, such as fast kinetics and high treatment capacity. Still, this process has many problems, such as high resins cost and resins regeneration requirement due to its fouling.
3. A membrane separation process is another extensively utilized wastewater treatment method. The recovery of heavy metal ions with high efficiency is possible with this technology; however, the disadvantages of this process include high membrane cost, membrane fouling, process complexity, as well as high operating costs, which have limited their use in heavy metal removal.
4. Furthermore, the adsorption technique for heavy metal removal is a relatively new practice. It has proven to be a great approach for reducing metal contamination. Furthermore, greater research into low-cost adsorption processes is needed to increase the large-scale utilization of non-conventional adsorbents. The usage of low-cost adsorbents can provide benefits such as cost reduction and increased heavy metal removal efficiency. Activated carbon's high cost prevents it from being used in adsorption. Activated carbons are expensive, and the regeneration process still has some issues. They can only remove a few micrograms of metal ions per gram of activated carbon. Overall, the two most important characteristics in determining the most likely adsorbent for heavy metal removal from wastewater are accessibility and price.
5. One of the most often utilized approaches is the electrochemical method, which is used to remove toxic effluents from contaminated wastewater and, according to a recent literature review, has emerged as a promising alternative to traditional methods of pollution treatment. Electrochemical treatment with electroplating wastewater showed complete removal of Cu, Cr, Zn, and Ni, while Ni and Pb removal ranged between 95 and 99%. Other metals which were present in lower concentrations were also effectively removed. This method is beneficial, including producing less sludge, having a high separation selectivity; it is regarded as quick and yields good reduction yields. This electrochemical treatment employs electrical energy to remove contaminants from water, reusing without chemicals. Furthermore, due to the short lifetime of electrode material, the utilization of electrochemical treatment in wastewater is limited.
6. AOP is now applied for the treatment of industrial wastewater because of its benefits, which include a strong oxidizer, rapid reaction rates, highly efficient, no secondary pollutant generation, and non-selective oxidation, which allows the treatment of several contaminants at the same time. For the elimination of harmful organic materials and heavy metals, it is a highly recommended approach. This technique has the potential to lower pollutant concentrations from hundreds of parts per million (ppm) to a few parts per billion (ppb). Furthermore, AOP systems utilizing  $H_2O_2$  should be carefully controlled for residual  $H_2O_2$  as it can have negative effects on subsequent treatment steps. However, by carefully designing the system, excess residual  $H_2O_2$  and any related repercussions can be avoided.

Although all of the above techniques can be based on some parameters such as pH, initial metal concentration, wastewater component, environmental impact, and economic parameters such as capital investment and operational costs, it is necessary to highlight that selecting the most appropriate treatment methods, the overall treatment performance compared to other technologies are all important considerations. Furthermore, plant flexibility, reliability, technological accessibility, and cost-effectiveness are important factors to consider when choosing the most appropriate and cost-effective treatment system for removing pollutants and protecting the environment.

**Author contribution** **Sonal Rajoria**: writing—original draft, data curation, conceptualization, investigation, validation. **Manish Vashishtha**: supervision, visualization, investigation. **Vikas K. Sangal**: supervision, visualization, investigation, writing—review and editing.

**Ethical approval**

Not applicable.

## Declarations

**Consent to participate** All participants gave informed consent to participate.

**Consent to publish** Not applicable.

**Conflict of interest** The authors declare no competing interests.

**Availability of data and materials** The datasets analyzed during the current study are available in the [Physical and Chemical Methods for Heavy Metal Removal]; Yadav M, Singh G, Jadeja RN (2021) Physical and Chemical Methods for Heavy Metal Removal. *Pollut Water Manag* 377–397. <https://doi.org/10.1002/9781119693635.ch15>; and [Electroplating Wastewater Treatment Method and Development Trend Analysis]; Lu BJ, Wu K (2020) Electroplating wastewater treatment method and development trend analysis. *Mater Sci Eng* 774. <https://doi.org/10.1088/1757-899X/774/1/012092>].

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